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Department of Earth and Planetary Sciences

Assessing Water Management of Mining Effluent Using Temporal and Spatial
Hydrologic Analyses

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Dedicated to the Department of Earth and Planetary Sciences
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Thanks for always rockin' hard.

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Abbreviations

500M : discharge pipe at Mineral Separation Plant
AHC : agglomerative hierarchical clustering
BASMIN : mining basin dredging pond
DO : Dissolved Oxygen (mg/L)
EC : Electrical Conductivity ($\mu\text{S}/\text{cm}$)
GDP : Gross Domestic Product
MMM : Mandromondromotra River
MSP : Mineral Separation Plant
Paddock 3 : storage basin for recycled water
Psu : practical salinity unit
QMM : QIT Madagascar Minerals
RWD : Raw Water Dam
S43 : drainage point into MMM river from WMC 703
S44 : drainage point into MMM river from WMC 803
SCC2 : control basin for effluent release points
TSS : Total Suspended Solids
WD 90 : Méandre River pumping station
WMC 703 : old effluent release point
WMC 803 : new effluent release point
WT : water temperature ($^{\circ}\text{C}$)

ABSTRACT

Associated with the commencement of any water-intensive mining operation is the formation of a set of policies, standards, and sampling protocols that guide the management of all water resources connected to the mining facility, surrounding environment, and affected communities. This study explores the interface between corporate water management and hydrologic methods by evaluating changes in water quality over the course of the mining cycle at Quebec Iron and Titanium (QIT) Madagascar Minerals in Tolagnaro, Madagascar. Field sampling and lab analyses of processed water were conducted following established QIT Madagascar Minerals (QMM) procedures and then compared to the complete QMM water quality database. Water quality is analyzed spatially to exhibit how processed water changes as it moves throughout the mining cycle before release into the environment. Spatial changes in various parameters exhibit initial deterioration in water quality relative to the source, mild improvement in quality before release as effluent, and natural remediation before discharge into the Mandromondromotra River. In addition, water quality parameters are evaluated temporally, revealing data gaps, the effects of seasonality, and the evolution of water quality monitoring practices at QMM. Technical evaluation of processed water as it flows through the mining system provides insight into how water monitoring and management can best be adapted at the corporate level to prevent negative impacts on the environment.

1. INTRODUCTION

Despite having less than half the area (587,041 km²) of many of its continental counterparts, the island of Madagascar is classified as one of eight biodiversity hotspots, with more species diversity than nearly all other countries in the world. What makes Madagascar particularly unique is the high percentage of endemism at the family, genus, and species level, consisting of the third greatest diversity of primates—all of which are endemic—260 bird species, and over 135 amphibian species (Sarrasin 2004). Even though this island nation has a rich supply of biodiversity and natural resources, it remains one of the poorest developing nations in the world. Approximately 80% of Madagascar's 16 million inhabitants live in rural areas and rely on the exploitation of natural resources to meet their daily needs (Vincelette et al. 2007). The unique biodiversity and community-dependence on natural resources necessitate that newly established corporations in Madagascar, such as QIT Madagascar Minerals (QMM), uphold a platform of environmental integrity and resource sustainability. Such a standard is especially important at the current site of QMM, just north of Tolagnaro (Fort-Dauphin) along the southeast coast of Madagascar, where community livelihoods are closely integrated with the sustainability of their natural resources and, consequentially, their water supply.

To explore the nexus amongst QMM, the environment, and regional hydrology, this study analyzes spatiotemporal water quality. Numerous studies have been conducted on the geochemistry of mining effluent at other sites throughout the world (Marques et al. 2011; Okumusoglo & Gunduz 2013; Nordstrom 2011; Varol et al. 2013; Odor et al. 1998; Waters & Webster-Brown 2013). Comparison to these studies, many of which focus on mining activities, aids the interpretation of the potential impacts of degraded water quality on the environment surrounding QMM. Physiochemical changes in water composition are commonly associated with

sand mining activities. The most dominant effect is lowering of pH and increase in sulfate concentration as a result of the oxidation of reduced sediments (Marques et al. 2011). In light of this trend, water quality at QMM is suspected to vary relative to its spatial distribution on the mining site, as its role in the ilmenite extraction process changes. Source water is expected to degrade in quality once onsite, with increasing concentrations of trace metals and higher acidity. QMM's physical treatment of processed wastewater should result in a decrease in turbidity, salinity, and total suspended solid values, as colloidal particles settle out of the water column. After release as effluent, water may be further remediated by filtration through soils (Sheoran 2005), attenuation of trace metals, and dissolution of other contaminants (Clemente et al. 2006; Braungardt 2003).

2. BACKGROUND

2.1. Presence of Rio Tinto in Southeastern Madagascar

As the largest mining operation in Madagascar's history, Rio Tinto and its subsidiary QIT Madagascar Minerals (QMM) have significant social, environmental, and economic impacts at a local, regional, and national scale (Seagle 2012). Rio Tinto is a joint, international corporation focused on exploration, mining, and processing of various earth mineral resources. Management responsibilities of the many Rio Tinto subsidiaries are shared by the company partners Rio Tinto plc, based out of London, and Rio Tinto Limited, based out of Australia. In the late 1980s, Rio Tinto plc established the mining subsidiary QMM, which is 80% owned by QIT Fer et Titane of Canada and 20% owned by the government of Madagascar. QMM explored the Anosy Region of southeast Madagascar for titanium dioxide (TiO₂) ore deposits for nearly 30 years before beginning a three-year construction phase (Yager 2010). Since mining operations began in May

2009, QMM and Rio Tinto affiliates have grown to cover ~40% of the global market for raw titanium dioxide, with QMM alone contributing 10% to the ilmenite market (Sarrasin 2004; Seagle 2012).

On a national scale, the economic benefits associated with the work of QMM are omnipresent. Before 2010, the combined mining and construction sector accounted for only 0.9% of overall GDP in Madagascar. Since the establishment of QMM, the mining and construction contribution to GDP increased 121%, with a 79% increase in ilmenite production, a 78% increase in rutile production, and an 81% increase in zircon (Yager 2010). Madagascar now contributes ~3% to total ilmenite stocks (Hayes 2011). QMM production and shipment is now operating at full capacity with the production of 750,000 tons/year of ilmenite and 40,000 tons/year of zircon. Despite the economic benefits, QMM production capacity and revenue streams have led to significant consequences for southeastern Madagascar as well.

Tolagnaro is one of the most isolated and least-developed regions in Madagascar. More than 80% of the population is occupied by subsistence agriculture, which contributes to a 2005 GDP level of \$309 USD per person. Only 54% of the urban population, and 4% in the surrounding rural villages, have access to potable water supplies. Average life expectancy is 52 years and the infant mortality rate is 89 per 1000 (Vincelette et al. 2007). The high level of poverty in the Anosy region translates into a high dependence on ecosystem resources to meet the demands of daily activities. Despite the unique biodiversity in this region, the local community continues to convert forestlands into agricultural fields. Local communities depend on the surrounding environment for everything from drinking water to food supplies to raw materials such as mahampy reeds (*Lepironia mucronata*), which are fashioned into mats for sale in the local markets, and timber, which is essential for construction needs (Lomberg 2011). This

socio-environmental relationship requires that QMM work to ensure the health of the water resources that support the environment local communities depend on. QMM has initiated several community-development projects to compensate for the environmental changes associated with the mine, including collaboration with the World Bank and JIRAMA (Madagascar National Water Company) to increase access to potable water in Fort Dauphin, and micro-economic projects for the neighboring villages of Mandromondromotra and Ampasy-Nahampoana (Seagle 2012; Pers. Obs).

2.2. Biodiversity and Natural Resources of Mandena

The coastal environment in the Anosy region is dominated by littoral forest ecosystems, which are believed to have once formed a continuous 1600-km band along most of Madagascar's eastern coast. With nearly 90% of original forest already lost due to human activities, the littoral forests now only exist as isolated remnant fragments (Consiglio 2006). Heavy mineral sands containing titanium dioxide, in the form of ilmenite and rutile, are unique to the sandy soils of the littoral forests near the QMM mining site at Mandena, some of the last remaining stands in the country. The surrounding littoral forests harbor a rich biodiversity with many endemic flora and fauna species, centering QMM operations in an environmentally sensitive area. Because the extraction process requires substantial supplies of water and the clearance of forests classified as having 'high conservation value', QMM is continually adapting their environmental management plans to keep pace with the outcomes of their mining practices (Vincelette et al. 2007).

The nature of heavy mineral extraction necessitates environmentally destructive processes including deforestation, soil disturbance, and watershed modification. In addition, the importance of water supplies throughout the mining cycle leads to potential environmental

effects related directly to hydrology and hydrogeology. Water issues that could be potentially caused by titanium dioxide mining include changes in flow and drainage patterns, siltation from increased sediment load of discharged process water, water table drawdown, erosion, and impacts on aquatic life from changes in water chemistry (Cundy 2009). The severity of these environmental effects could be further exacerbated by changes in climate. Current climate change projections for Madagascar predict higher average temperatures, changes in precipitation patterns, and increased storm intensity (Hannah 2008; Ingram 2005). For this reason, responsible water management practices should be implemented to ensure water quality and water flow dynamics remain consistent with the natural system and become adaptable to changing climate conditions.

2.3. Ilmenite Mining Process

Operations at QMM focus on the extraction of titanium dioxide derived from ilmenite (FeTiO_3) and rutile (TiO_2) ores, and the extraction of Zirsill (a combination of zircon, ZrO_2 , and sillimanite, Al_2SiO_5), found in heavy mineral black sands. Because TiO_2 (which is extracted from ilmenite and rutile) has a high refractive index (~ 2.61) it is an effective white pigment agent (Hayes 2011). Although rutile contains a greater concentration of titanium dioxide, ilmenite deposits are more common and more economically viable for extraction. The quality of ilmenite is divided into a chloride grade ($>58\%$ TiO_2 content) and a sulfate grade ($<58\%$ TiO_2), which influences the refining process that will be used on the ilmenite supply. The sulfate refining process involves the formation of titanyl sulfate from the ore using sulphuric acid ($\text{FeTiO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \text{TiOSO}_4 + \text{FeSO}_4 + 2\text{H}_2\text{O}$), and thereafter the hydrolysis of titanium dioxide ($\text{TiOSO}_4 + \text{OH}^- \rightarrow \text{TiO}_2 \cdot n(\text{H}_2\text{O}) + \text{H}_2\text{SO}_4$). The chloride process uses refines the

ilmenite with reaction in a chlorinator ($\text{TiO}_2 \text{ (impure)} + 2\text{Cl}_2 + \text{C} \rightarrow \text{TiCl}_4 + \text{CO}_2$) and then refined via an oxidation reaction $\text{TiCl}_4 + \text{O}_2 \rightarrow \text{TiO}_2 \text{ (pure)} + 2\text{Cl}_2$ (Reck & Richards 1997). Ilmenite mined by QMM is a chloride grade with >60% TiO_2 , making it a higher quality than many other sources (Hayes 2011; Pers. Comm. D. Bemana).

Ilmenite mining at QMM is a water-intensive process, incorporating a wet mining and dry mining cycle to separate out heavy minerals from black sands. During the wet mining process, sands are soaked in a large freshwater basin, dredged out, and mechanically separated on a wet gravity dock through a series of spirals. Sand is also extracted during a dry mining cycle. Following these two extraction processes and gravitational separation, ilmenite is further separated from other heavy minerals using magnetic and electrostatic methods. The final product is then transported 15km to Port d'Ehoala, where it is shipped to QIT Fer et Titane in Canada for refining and chloride processing (Hayes 2011; Sarrasin 2004).

2.3.1. Wet Mining Cycle

The wet mining cycle consists of a non-stop dredging process in an approximately 500 m x 300 m x 20 m dredging pond. A conventional cutter section dredge moves along a pre-determined circuit in the pond, stirring up sands at a rate of 3200 tons/hour (Lomberg 2011). The floating dredge extends to a maximum depth of 15 m. To increase the amount of sand extraction by the dredge, the pond level is lowered, which consequently lowers the water table (Pers. Comm. L. Rasolondrazao). Each year, 22 million tons of dredged sands are transported by pipe to the floating wet gravity circuit in the dredging pond (Point 4 in Figure 4).

2.3.2 *Dry Mining Cycle*

During the dry mining cycle, dry sands are mined from the surface and pumped with Méandre River water through a series of pipes directly to the floating separator. The surface sands are trapped after being pushed by heavy machinery into a ditch filled with low levels of water.

2.3.3 *Mechanical Separation Processes*

Heavy minerals are separated from sands in two steps. The initial step takes place on the floating concentrator in the dredging pond using gravity separation. The sands are passed through a series of large spirals in which different velocity flows separate dense heavy mineral concentrate (HMC) from less dense silica particles. The spiral circuits involve between four and six stages, including primary spirals, middling spirals, cleaner spirals, upgrade spirals, re-cleaner spirals, and scavenger spirals. The heavy minerals are separated in the spirals gravimetrically as they move to the inside of the trough, while the rest of the slurry travels down along the outside of the spiral channel (Fillipou & Hudon 2009). Silica sands are immediately returned to the deposit or used for construction of the sand walls that make up the discharge canal. This first separation results in 90% HMC and 10% residues. To separate out the residue the sands are piped to the Mineral Separation Plant (MSP) to enter a second separation process (Pers. Comm. L. Rasolondrazao).

2.3.4 *Physical Separation Processes*

At the MSP (Point 3 in Figure 4), heavy minerals are separated using electrostatic and magnetic fractionators. These physical processes separate conducting (ilmenite, zircon, rutile) and non-conducting minerals (silica sands). The residue monazite and silica tailings are returned to the deposit, while the ilmenite product is prepared at 60% grade TiO_2 for transport to Port d'Ehoala for export (Pers. Comm. L. Rasolondraza).

Following export to Canada, QMM's raw ilmenite is processed and prepared for sale as a pigment agent for whitening of paints (~60% of the global use), plastics, and paper (Hayes 2011). The smaller quantity of zirsill export (~12,600 t) is used for the production of ceramic tiles, television screens, and computer monitors (Fillipou & Hudon 2009). QMM's raw ilmenite export is a significant supplier to the global titanium dioxide market, valued around ~\$12 billion USD. The sustained profitability of QMM mineral production will depend on many factors, such as the political stability in Madagascar and the world demand for ilmenite (Yager 2010). Currently, annual demand for ilmenite is 5.3 million tons and is predicted to increase 3 - 4% annually until 2015, with developing countries constituting 70-80% of the demand (Hayes 2011; RDD 2010). The QMM mineral sands deposit contains approximately 1,900 million tons of mineable sand with total heavy mineral content of 4.5 wt%. Mining activities are projected to continue for more than 40 years (Dumouchel et al. 2005).

3. SITE DESCRIPTION

Madagascar is divided into four unique bioclimatic ecoregions, defined by distinct climate patterns that shape biological conditions (Irwin et al. 2010). This study takes place at

Mandena, 12 km north of the city of Tolagnaro (Fort Dauphin), which lies within the eastern lowland forest ecoregion. Since 2005, QMM has been operating on a 2000-hectare, littoral forest-dominated, ilmenite deposit located in this region (Vincelette et al. 2007). Two other QMM mining initiatives have been proposed for Petriky and Sainte-Luce, to the north of Mandena. The Mandena site is situated on coastal plains stretching 6 km E-W and 4.5 km N-S, bordered by the Indian Ocean to the south and the Vohimena Mountains to the northwest (Lomberg 2011). In addition, Mandena is bordered to the south by a complex lagoon system and coastal barrier. According to pre-exploitation surveying by Rio Tinto, the site lies on 75% open lands, 10% highly degraded forest, and 15% wetlands (Vincelette et al. 2007).

3.1. Geology

The stratigraphy of the coastal plains of Mandena are composed of littoral sands and alluvial sediments overlying an ~18 m thick mineralized sand layer, a laterite substratum, and cordierite gneiss bedrock (Vincelette et al. 2007). Figure 1a shows the primary geologic units of Tolagnaro and the surrounding southeastern region of Madagascar. The sands are placer deposits, formed during the marine transgression-regression cycles of the late Pleistocene Epoch (~150,000-80,000 yrs). The constant reworking of the sands as a result of these sea cycles led to the accumulation of valuable heavy minerals. The heavy minerals form as a result of gravimetric settling of more dense materials and the chemical/mechanical resistance of minerals during sedimentary processes (Stanaway 2012).

There are several models for the accumulation of placer deposits, which are dependent on the geology and fluid flow regime of the region. The southeastern Madagascar ilmenite-zircon placers are characterized as Type-C regressional beach placers (Dumouchel et al. 2005; Roy

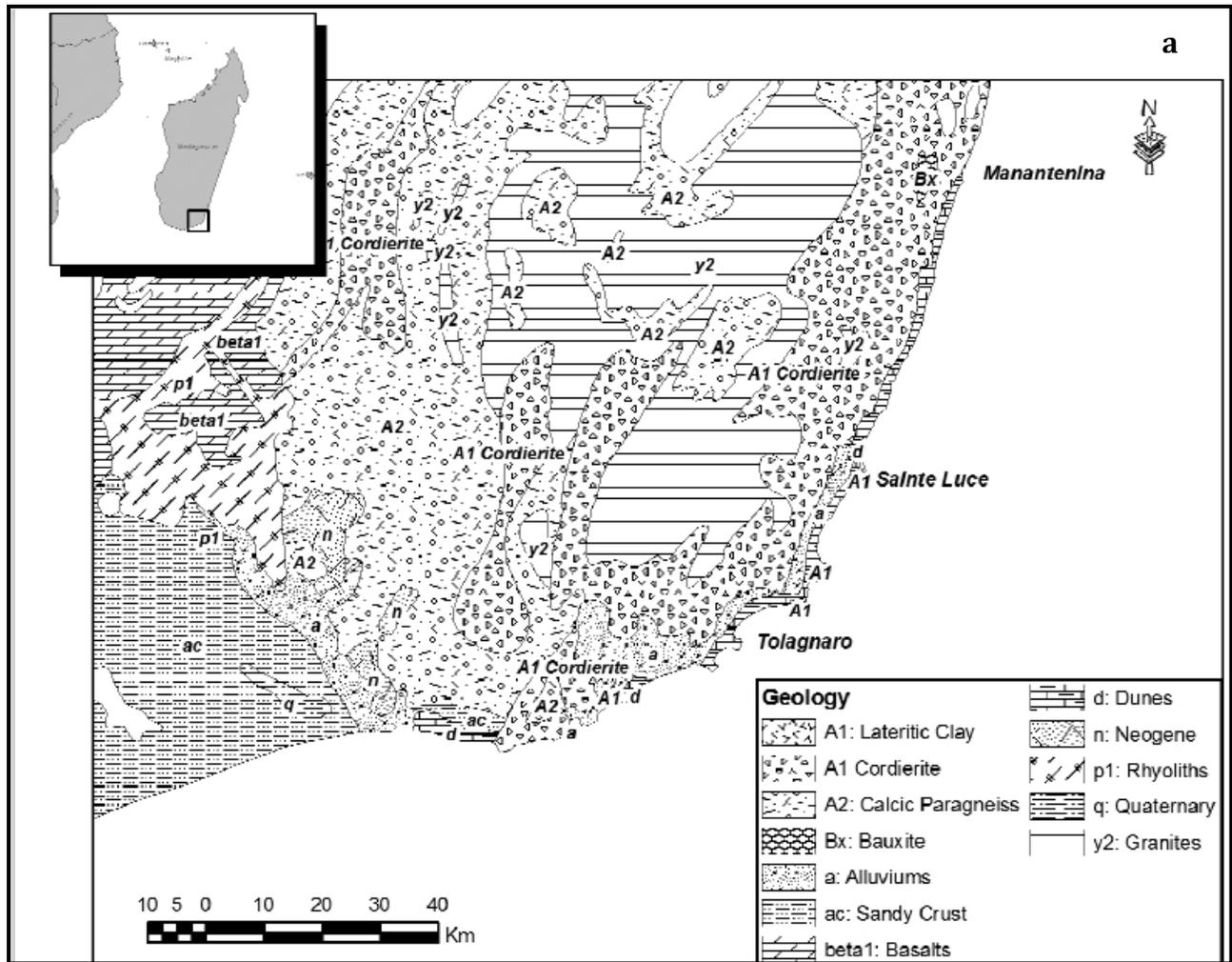
1998). This type of deposit is typical of regions with prograded beach ridge plains aligned with the coast, consisting of accreting beach berms. Regressional beach placers are formed as the shoreline advances and the sea retreats, depositing sands from the seafloor, long-shore drift, and/or biogenic debris. Asymmetrical shoaling waves push coarser and denser mineral grains up the shoreface, causing the accumulation of heavy minerals (Stanaway 2012). The Mandena deposit is classified as Type-C because the placers accumulate during *episodic* shoaling wave access to tidal delta sands and offshore ridges containing locally weathered, mineral-rich metamorphic rock (Roy 1998).

Fort Dauphin is in a unique location, typified by volcanics and metamorphic facies of the Neoproterozoic/Cambrian East African Orogen, and the Anosyan Belt. The Anosyan Belt is made up of cordierite-garnet leptynites, charnockites, rare pyroxenites, granites, and mylonitic gneiss. Radioactive, detrital monazite grains, containing significant amounts of U-Th, are also present in the region due to erosion of granites and charnockites with biotite-rich layers bearing large monazite crystals (Dumouchel et al. 2005; Montel et al. 2011). Pegmatites and syenites, formed from melting of silicocarbonatitic crusts during the Pan-African collision (c. 515 Ma), are a regional source of phlogopite, diopside, calcite, and anhydrite (Morteani et al. 2013; Schenk et al. 2011; Boulvais et al. 1998). Coastal sediments contain laterite and bauxite grains (Montel et al. 2011).

3.2. Climate

Orographic effects of the southeast trade winds, monsoonal winds, and occasional periods of cyclone activity influence regional climate. Seasonality is characterized by a wet period of heavy rainfall (November to May) and a dry period (June to October). During the dry

season average monthly precipitation values range from 75-150 mm, while during the wet season monthly averages range from 165-290 mm and account for 70% of annual precipitation (Lomberg 2011; Vincelette et al. 2007). The dry season experiences colder temperatures and the wet season warmer temperatures, with an annual average temperature of 23.7°C. Detailed precipitation data for Madagascar is only represented by a monthly average of rain gage measurements from the capital city, Antananarivo (Figure 2).



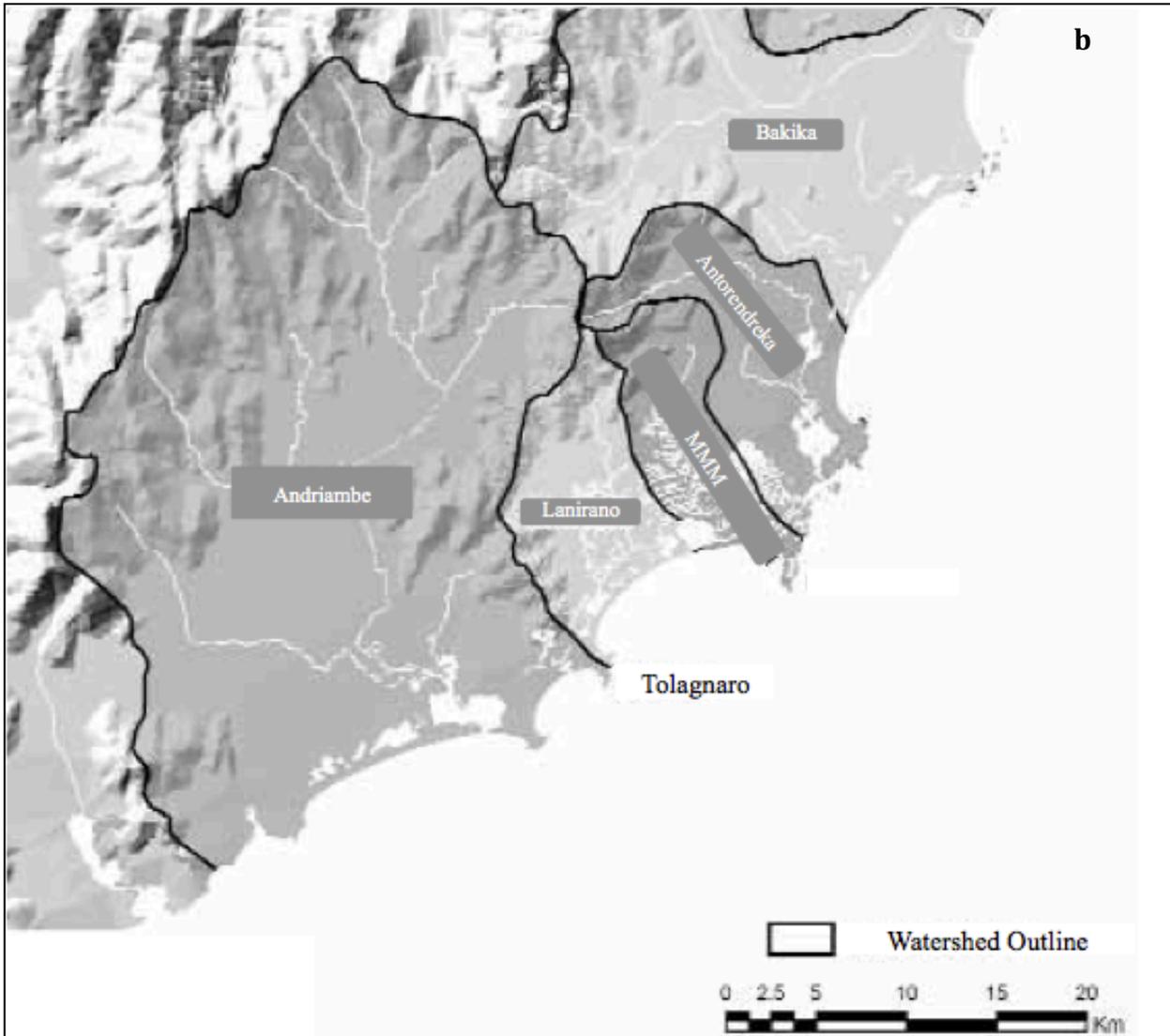


Figure 1 a. Geology of southeastern Madagascar **b.** Catchment hydrology of the Mandena mine site. MMM represents the Mandromondromotra watershed. Mandena is based on the Lanirano and MMM watersheds. (Vincelette et al. 2007).

3.3. Hydrology

The Mandena watershed covers two primary river catchments: the Mandromondramotra (MMM) catchment and the Lanirano catchment. The MMM River flows along the northeast border of the mine and discharges into Lake Ambavarano to the southeast. The MMM catchment is hydraulically linked to the Mandena aquifer system and includes the Méandre River.

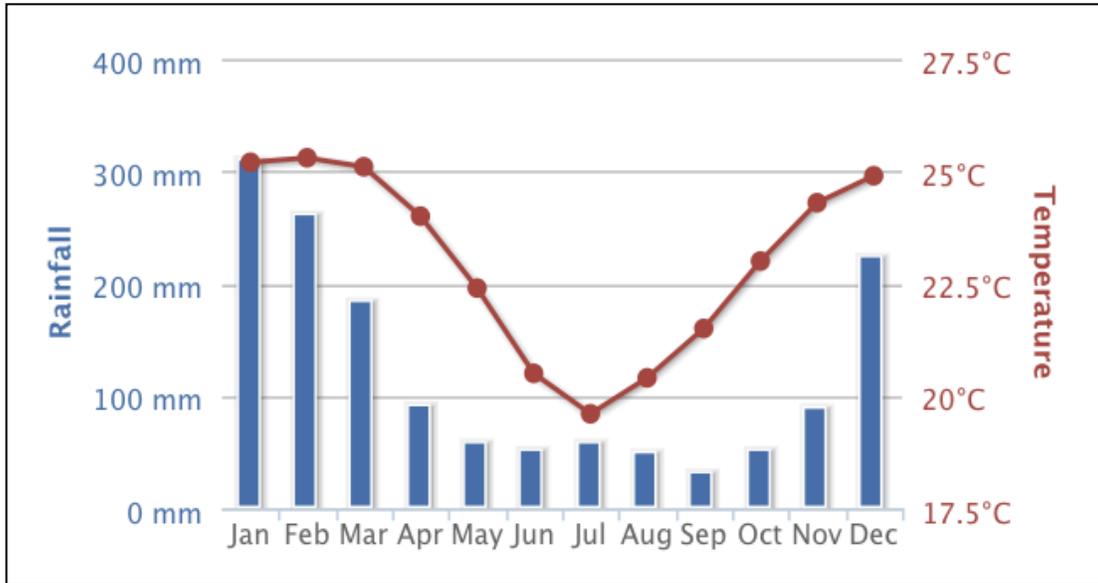


Figure 2 Average monthly precipitation data for Madagascar between 1990 and 2009 (World Bank 2013).

The Lanirano catchment includes the Antinosoro, Anandrano, and Lanirano Rivers, all of which discharge into Lake Lanirano in the south (Vincelette et al. 2007). Formerly, water used for processing at the mine was sourced from the Méandre River that flows S-N along the southern border of the mine. This changed when QMM began recycling all water resources through an onsite, closed-loop system beginning in late 2012 (Pers. Comm. L. Rasolondrazao). Due to highly variable precipitation patterns and the braided river system at Mandena, changes in water table and surface water levels are unpredictable and make assuring effluent water quality difficult. In addition, the proximity of Mandena to the ocean makes the site susceptible to saltwater intrusion from the inundation of tides (Pers. Comm. L. Rasolondrazao). Shallow water tables, the proximity to the coast, and the complex surface water system support an interdunal wetland ecosystem with rich biodiversity (Vincelette et al. 2007).

4. METHODOLOGY

4.1. Terminology

Before explaining the methods used to evaluate the ilmenite mining hydrologic system, it is necessary to have a clear understanding of the terms used throughout this study to classify water types throughout the mining process. Water is a critical element at every point throughout the ilmenite mining cycle, yet its role and chemical composition varies at different steps throughout the process (Figure 3). To clarify these changing characteristics, the hydrological system has been divided into four categories: source water, processed water, effluent, and remediated water. *Source water* refers to the bodies of water that supply the dredging pond and Mineral Separation Plant (MSP). Source water for QMM includes water pumped from the Méandre River and water recycled back through the system from the onsite basin, Paddock 3. *Processed water* refers to water that comes into direct contact with the raw mining material, intermediate product, finished product, byproduct, or waste product, at any point during mining or processing. Typically, effluent is any treated or untreated wastewater that is released by an industrial system into surface waters. For this study, *effluent* refers to water that is discharged into the surrounding watershed from release points WMC 703 and WMC 803. *Remediated water* will be the term used to describe the water that flows from the effluent release stations into the MMM River sampling points S43 and S44, after being treated industrially and naturally.

A further delineation is made between polluted waters and natural waters. *Natural waters* are those that lie within established potable water standards, characterized by circumneutral pH, minimal suspended solids, and low levels of pollutants, trace metals, and dissolved ions. Natural or anthropogenic processes may cause waters to become *polluted* and fall outside acceptable

limits for potable water. *Polluted waters* are typically distinguished by low pH, high turbidity, and abnormal levels of mobilized metals or dissolved ions.

Several key physiochemical parameters also invite explanation, including electrical conductivity ($\mu\text{S}/\text{cm}$), dissolved oxygen (% saturation and mg/l), total suspended solids (TSS), and chemical oxygen demand (COD). Electrical conductivity (EC) is a measure of the electrical current carried by the movement of ions in a solution, or the reciprocal of resistivity. EC depends on the ions that are present in a solution and their concentration, thus conductivity can serve as an indirect measure of total dissolved solids, total ionized solids, or salinity in a water sample. For example, high conductivity values indicate a high concentration of dissolved solids because more ions are available to conduct electricity (Girard 2014). The concentration of dissolved oxygen (DO) in water is a mass measurement in milligrams per liter. Despite its susceptibility to environmental conditions, DO measurements provide a useful tool for evaluating the health of a water body. In most cases for surface waters, high DO concentrations reflect good water quality, and low DO concentrations (<3 mg/L) are indicative of poor water quality. TSS is a metric representing the presence of suspended and dissolved solids in the water column, and is thus directly related to conductivity and turbidity. Elevated TSS levels of effluent have a deteriorating effect on aquatic life when discharged into the environment (Bilotta & Brazier 2008). COD is a measurement of the susceptibility of organic substances in a water sample to oxidation by acidified potassium dichromate at 100°C and is used to determine the amount of organic pollutants in surface water (Girard 2014). All of these measurements are essential for evaluating the changes in surface water quality as it progresses through the mine.

4.2 Data Collection

Methods used throughout this study are separated into four main components: field sampling, follow-up lab analyses, interpretation of an existing database of hydrologic parameters, and statistical analyses. Each analytical tool, described in detail below, was essential to forming a comprehensive evaluation of the water management and monitoring regime of the *Service de L'Eau* at QMM, since operations commenced in 2009.

One of the objectives of this study is to evaluate the strong and weak points of QMM's water management, which includes the water monitoring practices of the *Service de l'Eau*. The hydrological sampling procedures used by the mine were followed in order to evaluate the company's sampling methodology and technical analyses.

4.2.1. Field Sampling

Hydrological sampling was conducted over the course of the mining process to understand changes in water quality and flow (Figure 3). Based upon expectations for variation in water quality dependent on spatial locale, sites were chosen near source water, at various sites on the mining complex, and at the points where effluent is discharged into the surrounding environment. Samples for the original source water site were taken from the Méandre River (sample ID: WD90), and from the recycled water storage basin (sample ID: Paddock 3). Samples on the mining complex were taken halfway between the dredge and wet mine flotation dock in the dredging basin (sample ID: BASMIN), a point of control for canal release (sample ID: SCC2), and the point of release from the mineral separation facility-MSP (sample ID: 500M). Finally, field samples were taken from two of the three water release points (sample ID: WMC803 and WMC703). QMM conducts weekly sampling of processed water; therefore three

sample sets were collected over the course of this study (April 2013) while accompanied by a team of two technicians in the *Service de l'Eau*.

Parameters evaluated in the field included temperature (°C), pH, electrical conductivity (µS/cm), dissolved oxygen (% saturation and mg/l), and turbidity (NTU). The temperature, pH, and electrical conductivity were measured using a Hanna HI 98311 multi-purpose meter.

Dissolved oxygen was measured using a SPER Scientific 850045 DO Meter and turbidity using a HACH 2100Q Portable Turbidimeter. In addition, water samples were collected at each site in a 1L clean, borosilicate glass container for later lab analyses of oils and greases, as well as a 1.5 L plastic container to store samples for all other lab analyses.

4.2.2 Laboratory Analyses

Following physical sampling, several chemical analyses for each point were conducted onsite in QMM laboratory facilities. In the QMM laboratory analyses of salinity, total suspended solids (mg/l), total dissolved solids (mg/L), dissolved ions (sulfates, ammonium, calcium), trace metals (nickel, aluminum, zinc), and the chemical oxygen demand (COD) were conducted on each field sample. Standard analytical procedures were followed for these analyses. For the total suspended solids, each sample was filtered through a filtration pump with 47mm micro-fiberglass Whatman filters and then dried in a lab oven at 105°C for one hour. The concentration of total suspended solids was calculated with the dry sample as follows:

$$TSS = \frac{M_{105} - M_0}{V_{sample}} \times 100$$

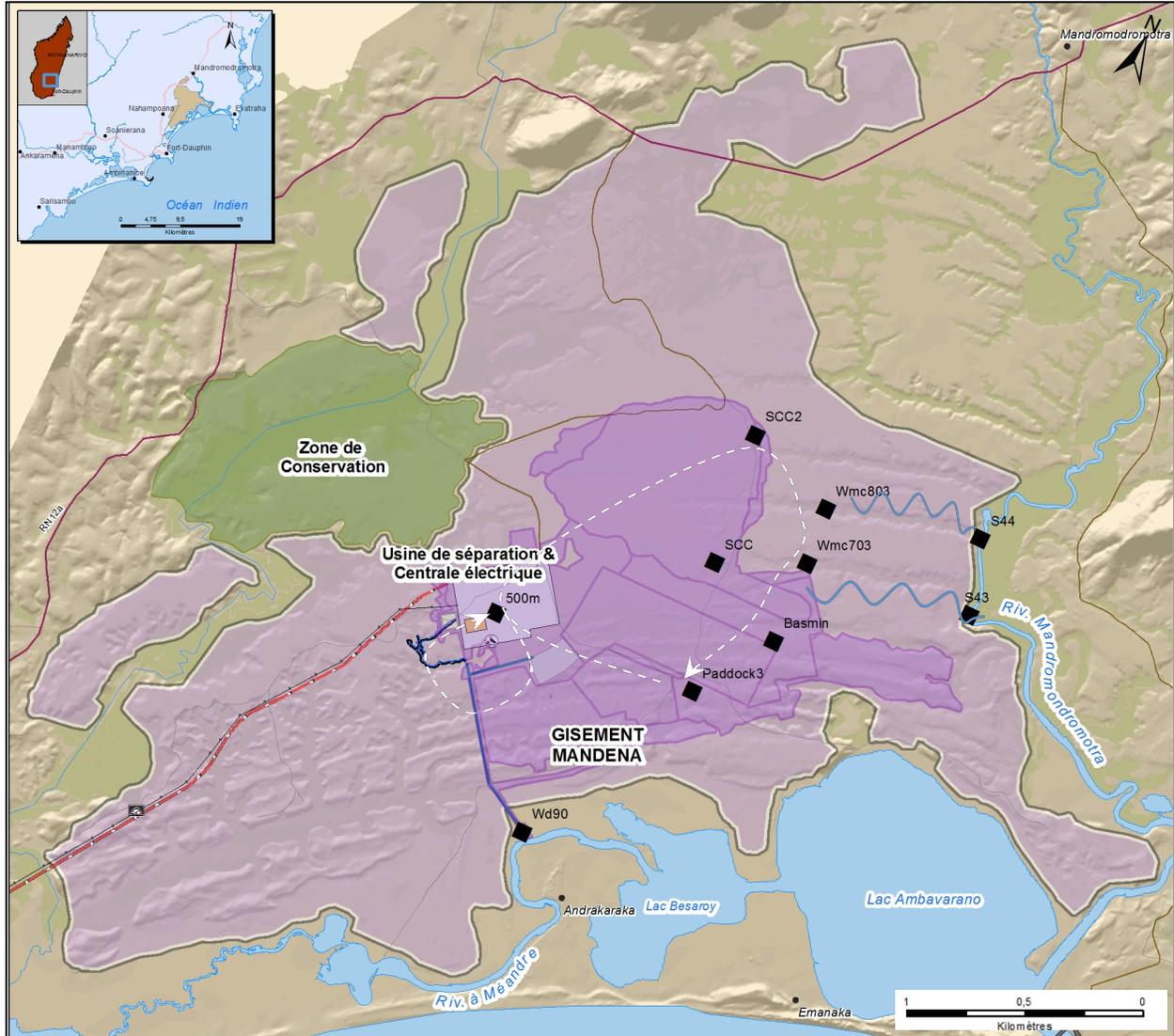


Figure 3 Map of the Mandena mining site marking the geographic location of the seven sampling sites (WD90, 500M, Paddock 3, Basmin, SCC2, WMC 703, and WMC 803). The yellow shaded region in the inset corresponds to the light shaded purple region shown on the large map. The light purple is the extent of the ilmenite placer deposit. S43 marks the watershed flow point for WMC703 and S44 marks the discharge point for WMC803. The light blue wavy lines connecting the effluent discharge points to S43 and S44 represent the diffusive down-gradient transport of the discharged water through the wetland ecosystem. There is no pipeline connecting wastewater to the MMM River, discharge follows natural drainage patterns when released. Dark purple outlined regions are representative of different positioning of the mine, which has progressed south to north since operations began in 2009. The dark blue line is the primary pipeline that carried Méandre River source water to the mine, before the mine transitioned to water recycling. Green-shaded zones represent the surrounding natural wetlands. The dashed white lines trace the flow path of water during the mining process. Water is sourced from an onsite storage basin (Paddock 3) where it is transported for processing of sands at the MSP (500M). From the MSP it is either recycled through the smaller loop into a smaller holding pond and reused at MSP, or it flows through the larger loop, collector canal system for treatment. The collector canal flows through the biodiversity control pond (SCC2) and past the two effluent release points (WMC703, WMC803), where water is discharged depending on quality. If the processed water is determined to be too poor of quality for discharge it flows to the dredging pond (BASMIN), which drains into Paddock 3.

where M_{105} is the mass of the dried sample (mg), M_0 is the mass of the filter, and V is the volume of the sample (L). The pH and temperature were recorded using a Hanna 98150 pH/ORP Meter, dissolved oxygen with an YSI 5000 DO Meter, turbidity with a Turbiquant 1100 IR Turbidimeter, and salinity with a H19828 Hanna multi-purpose meter. The dissolved ions (calcium and sulfate) were analyzed using ion chromatography methods with a Metrohm 881 Compact IC Pro. The trace metals were evaluated using ICP Optical Emissions Spectrometry with an Agilent 700 Series ICP-OES. COD was evaluated using Merck Spectroquant COD test kits, in which 2 mL of each sample was placed in a Spectroquant test tube, incubated at 150°C for two hours, and then measured at high range (<1500 mg/L) on a DR 2800 Portable Spectrophotometer.

Ammonium concentrations were measured using a Metrohm 848 Titrino Plus titrator. To prepare the samples, 100 mL of sample and 25 mL of sodium hydroxide were distilled for five minutes with 50 mL of 2% boric acid in a BUCHI K-350 Distillation Unit. After calibrating the titrator with solutions of pH 4, 7, and 10, a standard of distilled water and 2 mg/L ammonium solution was measured. For each standard and sample, the solution was stirred for 30 seconds before the measurement began.

4.3 Analysis of Secondary Data

For a comprehensive picture of the hydrological setting, collected data is analyzed in conjunction with company data provided by the *Service de l'Eau*. From this compilation, the study aims to draw conclusions about the impact of discharged wastewater on the surrounding environment. The overall quality of processed wastewater at QMM is analyzed using spatial and temporal comparisons. Water quality parameters are gauged spatially by comparing

physiochemical and laboratory data from various sites on the mine. For the temporal evaluation, water quality data stemming from when QMM operations began in November 2009, is compared annually and averaged monthly.

All data for sampling site SCC (November 2009 – September 2011) and SCC2 (October 2011 – Present) are combined to create a more complete record. SCC and SCC2 represent two control points along the discharge canal. Sampling at SCC ceased as the mine migrated, making data collection from this site extraneous.

4.4 Statistical Analyses

Multivariate statistics are an effective tool for interpretation of multidimensional hydrochemical and physical measurements (Vega et al. 1998). Correlation analyses are used to analyze covariance of water quality parameters and determine which geochemical effects to water quality are statistically significant. The linear relationship between variables is tested using Pearson correlation with statistical significance $p < 0.05$ (Gotway et al. 1994). To calculate the Pearson matrix, the data is standardized between -1 and 1 and then divided by the standard deviation of the parameter to find the correlation coefficient r (Appendix C).

In addition to the correlation matrix, agglomerative hierarchical clustering (AHC) is used to determine the underlying behavior of water quality data and to spatially reduce the sampling sites into smaller homogenous groups that share similar chemical characteristics (Gonçalves & Alpium 2011). Similar to the method of principle component analysis, in which principle components are determined from variable similarity, AHC is an unsupervised pattern recognition technique that clusters based upon the normalized distance between variables (Vega et al. 1998). In this study, the dissimilarity was calculated using squared Euclidean distance and agglomerated

using Ward's methods (Appendix D).

5. RESULTS

The results below are offered in several ways to highlight the strengths and weaknesses of water management at QMM. Compiled results consist of a description of water flow at Mandena, a compilation of water quality data based on site location, and statistical and graphical representation of annual and monthly variations in water quality. The diversity of results produces an encompassing perspective of the QMM water management and monitoring regime.

5.1. Flow of Water Resources at QMM

One of the primary objectives of this study is to understand how water is used by QMM at each step in the mining cycle. Only after acquiring context about the hydrological system by touring the mine facilities, visiting processed water sampling locations, and talking with technicians from the *Service de l'Eau*, were conclusions drawn about the strengths and weaknesses of water management at QMM.

The array of field sampling sites used for physiochemical analyses of water quality cover the most critical hydrological steps in the mining process (Figure 4). Below is a stepwise description of water flow at the Mandena mining facility, focusing on its transformation at and between each sampling locality. The explanation is divided based upon the evolution of water, as distinguished by its function: source water, processed water, effluent, and remediated water. The hydrological network at QMM is best characterized as a dual closed-loop, open system. The piping system consists of one loop connecting the RWD to the MSP, and a larger loop that circles around the perimeter of the site, passing through BASMIN, the effluent release points, the

MSP, and consisting of the full collector canal system. The system is considered open because there are no barriers between the hydrological system on site and the surrounding wetland ecosystem. Water passing through the loops can overflow its banks and is eventually released as effluent into the environment.

5.1.1. Source Water

Before June 2012, the path of water for the Mandena mine began at the Méandre River, located southeast of the mine center (Point 1 in Figure 3). Formerly, the Méandre River was the source for nearly all water used for heavy mineral separation and extraction. A pump station was built by QMM along the riverbed, which has a pumping capacity of ~20,000m³/day of water to the mine (Lomberg 2011). A royalty was paid to the Madagascar Authority of Water and Sanitation for every cubic meter of water taken from the river (Pers. Comm. Rasolondrazao). Due to economic and environmental considerations, QMM began recycling water to the mineral separation plant and dredging pond, rather than pumping it from the river. After pumping, water travelled via a series of steel pipes to either the MSP or the dredging pond (Pers. Comm. Bemana).

Currently, 100% of water used by QMM is recycled through a closed loop system of pipelines, canals, and manmade basins. The recycled water sources from two sites: 80% from Paddock 3 (Point 2 in Figure 3), a man-made storage basin built at the end of 2012, and 20% from a raw water dam (RWD), built in a lined dune depression adjacent to the MSP. The RWD is only connected to the MSP as part of a small, closed loop pipe system. From Paddock 3, water is piped directly to the MSP or the RWD. The reliance of QMM's open system on natural replenishment requires close monitoring of seasonal variation. For example, a series of pipes

from the RWD prevents dam overflow during the rainy season by diverting water to the canal system. Recycled water is replenished naturally by rainfall or groundwater infiltration (Pers. Comm. RASOLONDRAZAO). Because the use of recycled water for mining processes is a relatively new initiative at QMM, the management of this system is still evolving.

5.1.2. *Processed Water*

Source water becomes classified as processed water when it is used for heavy mineral separation, sand transport, or other TiO_2 processing purposes. After transport by pipeline from Paddock 3 to the MSP, recycled water is used in the Feed Preparation circuit for attritioning of heavy mineral concentrate (HMC). During the *attritioning* process, HMC sand particle surfaces are cleaned to increase the efficiency of electrostatic separation and minimize dust levels at the MSP (Fillipou & Hudon 2009). With attritioning HMC is upgraded from the gravity separation heavy minerals content of 90% to 95% heavy minerals content (Dumouchel et al. 2005). 500M, where processed wastewater is released from the MSP (Point 3 in Figure 4), represents the next stage in the water cycle at QMM. Processed water is released from point 500M into a two-way canal system, flowing southwest in one direction to the raw water dam (RWD) loop or northeast to a 4 km-long collector canal system. Each loop connected to the MSP includes a pumping station managed by the MSP operations team, in order to control the quantity of water entering each system (Lomberg 2011). The relative percentage of water discharged into each canal is a function of wastewater outflow and water quality. If the water quality of 500M discharge is poor, a higher percentage of water is discharged into the collector canal system to allow for remediation before reuse in the attritioning process (Pers. Comm. D. Bemana).

Processed wastewater that does not return to the RWD is released into the collector canal loop. The collector canal is a 4 km, unlined seepage canal that loops through and around the mine site. The canal serves as a natural treatment system for processed wastewater and mine tailings (i.e. waste sands). Mining activities result in a high concentration of colloidal-sized particles and thus a high value of total suspended solids. As processed water moves through the canal system at low velocity, suspended sediments either filter through the sand or settle onto the canal bed (Lomberg 2011; Pers. Comm. D. Bemana).

Processed water first flows through the canal from 500M to the canal control point (SCC2, Point 5 in Figure 4). If the level of TSS has been sufficiently remediated, processed water is released through five pipes to another canal leading to effluent release points WMC803 and WMC 703. If water quality remains poor, the processed water is fed via four pipes into the rest of the collector canal. SCC2 (formerly referred to as the biodiversity pond) serves as another means to ensure processed water will not have an impact on the surrounding environment. Studies on the aquatic life in SCC2 are occasionally conducted, in addition to weekly physiochemical analyses collected at the outlet point of the pond (Lomberg 2011; Pers. Comm. D. Bemana).

Processed water not released to WMC803 or WMC703 continues to move through the collector canal and drop sediment. The next divergence point in the canal carries processed water to the dredging pond or back to Paddock 3. Again, if water quality is poor it is diverted to the dredging basin (BASMIN, Point 4 in Figure 4) for hydraulic mining of ilmenite. Approximately 72,000 m³ of water is used each day for dredging and separation activities to dredge ~0.15-0.30 ha of sand (EMP 2001). The maximum dredging depth of 15 m is extended by lowering the BASMIN water level, resulting in a ~1-4 m lowering of the water table (EMP 2001; Pers. Comm.

L. Rasolondrazao). If processed water in the collector canal has been remediated, it is diverted into Paddock 3 instead of BASMIN. From Paddock 3, water begins to cycle through the mine once again.

5.1.3. Effluent

Water approved for release from SCC2 drains toward two other monitoring points adjacent to effluent discharge points. The original release point is WMC 703 (Point 6 in Figure 4) and the newer release point, constructed in November 2011, is WMC 803 (Point 7 in Figure 4). Flow of processed water towards these points allows for suspended solids to drop to the canal bed and for water to be properly oxygenated before release. If water quality meets QMM/State of Madagascar approved standards (Table 1), five pipelines are opened from WMC703 and/or seven pipelines are opened from WMC803 to release effluent into surrounding wetlands.

Effluent is typically only released if it meets background water quality criteria, if there is excess mine water in the canal, or if there is no observed impact on biodiversity (Lomberg 2011). However, QMM has received approval from the State of Madagascar to release effluent even if the pH is below the 6.0 – 8.2 range. The quantity released varies depending on precipitation levels and groundwater inflow.

Field Parameter	Target Value
Color	<40 Pt-Co
pH	6.0 - 8.2
Dissolved Oxygen	> 5 mg/L
Total Suspended Solids	< 100 mg/L
Electrical Conductivity	< 350 μ S/cm
Chemical Oxygen Demand	< 20 mg/L

Table 1 Target values for effluent of key field parameters, established by QMM and the State of Madagascar as of May 2013 (Pers. Comm. L. Rasolondrazao; Lomberg 2011). Classification of color follows the platinum-cobalt scale (Pt-Co).



Figure 4 Sampling schematic for hydrological field study of processed water at QMM. Numbered points represent each sampling location visited during this study: 1- source water from the Méandre River (WD90); 2- source water from onsite basin (Paddock 3); 3- processed water from mineral separation plant (500M); 4- processed water from dredging pond (BASMIN); 5- effluent from canal control pond (SCC2); 6- effluent discharged from old water release point (WMC703); and 7- effluent discharged from new water release point (WMC803).

5.1.4. Remediated Water

As effluent flows away from the WMC703 and WMC803 release points, the water is remediated naturally by filtration and drainage through the surrounding estuarine system before discharge into the MMM River. WMC703 effluent drains from the wetland into the MMM River at site S43 (Point 7 in Figure 4) and WMC803 effluent drains into the MMM River at S44 (Point 8 in Figure 4). The effluent quality improves further by dilution in the MMM River before it discharges into Lake Ambavarano (Lomberg 2011). The difficulty of sampling in the MMM River, which requires the use of a boat, limits monitoring capacity at S43 and S44.

5.2 Spatial Variation in Water Quality at QMM

Spatial changes in water quality parameters during April-May 2013 provide a temporal snapshot of the environmental geochemistry at the Mandena facility. The parameters evaluated for this spatial analysis include physiochemical measurements collected in the field (temperature, pH), physiochemical measurements analyzed in the lab (EC, DO, TSS, COD), trace metal analyses (Zn, Ni, Al), and dissolved ion concentrations (NH_4^+ , SO_4^{2-} , Ca^{2+}). The data collected (Appendix B) were used to plot parametric values for the Méandre River source water (WD90), recycled source water (Paddock 3), mineral separation plant discharge water (500M), dredging pond water (BASMIN), canal control basin (SCC2), and two discharge points (WMC 703, WMC 803). Analysis of MMM River release points (S43, S44) was limited to historical data from February 2013 due to the lack of sampling consistency by QMM's *Service de l'Eau* for these sites.

Divergence or covariance of water quality parameters at different sampling sites provide insight into the causes of water quality changes and underlines the diverse impacts discharged

processed water can have on the environment (Figure 5). The control site (WD90) represents the sampling point with physiochemical properties of a natural, healthy hydrological system. In comparison to other sites, the control site WD90 is less acidic ($\text{pH} \approx 6.3$) and has lower concentrations of trace metals and ionic substances. Paddock 3, the current source of recycled water for the MSP and the dredging basin, has DO, TSS, and COD values similar to the control site, lower pH values, and higher values for all other parameters. There is a large anomaly with the spatial trend in TSS, with a $>4000 \text{ mg/L}$ jump in concentration at SCC2. The dissolved ion and trace metal concentrations follow a similar pattern, with a significant increase in concentration relative to WD90, stable levels at onsite locations, declining levels at release points, and low concentrations at MMM River discharge points. The pH values do not recover to the same level as WD90, remaining acidic even at the watershed discharge points. Correlation amongst water quality variables across all sites is discussed in further detail in Section 5.

In the most general sense, water quality deteriorates as it transitions from source water to processed water. Before release as effluent from WMC 803 and WMC 703, processed water is partially remediated as suspended colloids settle to the collector canal streambed. At the final stage, when discharged into the MMM river, water quality is almost completely remediated to a physiochemical level similar to that of the Méandre River.

5.3 Temporal Variation in Water Quality at QMM

Data provided by the *Service de l'Eau* was used to understand how water quality has varied over time. Temporal analyses highlight annual changes in processed water quality at points of interest onsite, quality of processed water relative to established standards, seasonality effects, and data gaps in sampling frequency.

5.3.1 Annual Comparison by Water Quality Parameter and Sampling Site

For effective interpretation of annual variations in processed wastewater quality, physiochemical parameters classified as a primary concern by QMM, pH, dissolved oxygen (DO), total suspended solids (TSS), and secondary concern, electrical conductivity (EC), are evaluated. In addition, field measurements for water temperature are graphed to account for its potential effects on other parameter values. Although fewer variables are compared at an annual scale, comparison of the aforementioned fundamental variables exhibit the effects of seasonality and changes in anthropogenic influence on water quality as QMM evolved and developed its monitoring practices. Physiochemical and laboratory results are sourced from QMM databases. The frequency of sampling and lab analyses for each parameter vary; therefore, a monthly average is calculated. Data gaps reflect changes in sampling and analysis frequency associated with the evolving water management regime of the mine. Water quality measurements are used to highlight annual variations by site (Figure 6) and by parameter (Figure 7). Annual comparisons of the five parameters are generated for each site (Appendix A).

Covariance of parameters from year to year highlights the effect of seasonality on the water quality parameters within the dredging pond at QMM. Each year there tends to be lower values of EC, DO, and pH during the cold, dry period (June to October), and relatively higher values during the wet period (November to May). Changes in temperature associated with season typically affect DO levels as well. This is due to the fact that dissolved oxygen in surface water is controlled by temperature, with cold water capable of holding more dissolved oxygen than warm water (Girard 2014). The DO measurements from this study were not consistent with this trend, insinuating that factors other than seasonality are impacting DO. Annual comparisons are

useful when differentiating changes in water quality caused by mining practices versus changes caused by climatic conditions. Note that sampling for the dredging pond was not required until 2011.

Evaluating one parameter, such as dissolved oxygen (Figure 7), temporally across all sites places annual changes in a spatial context. For dissolved oxygen levels across the mine, there is evidence that the values are lower onsite, increase slightly at canal effluent points, and increase again at river discharge points. In addition, an annual site comparison of DO reveals gaps in data collection. Data gaps are a result of inconsistent monitoring and evolving sampling protocols required by QMM.

5.3.2. Monthly Comparison by Water Quality Parameter, Sampling Site, and Standard

Monthly comparisons of average values for pH, dissolved oxygen, electrical conductivity, sulfate concentration, and aluminum concentration serve as a check on water quality relative to established standards and highlight the evolution of the water management regime at QMM (Figures 8-12). The start of sampling periods varies due to changes in water monitoring requirements necessitated by QMM and the government of Madagascar (Pers. Comm. L. Rasolondrazao). Data series are generated for one parameter at each sampling site and analyzed over time, in order to compare variations in physiochemical parameters relative to the course of water throughout the mine. To assess whether a parameter falls within required water quality limits, parameter values are compared to wastewater effluent standards established by the government of Madagascar and Rio Tinto QMM.

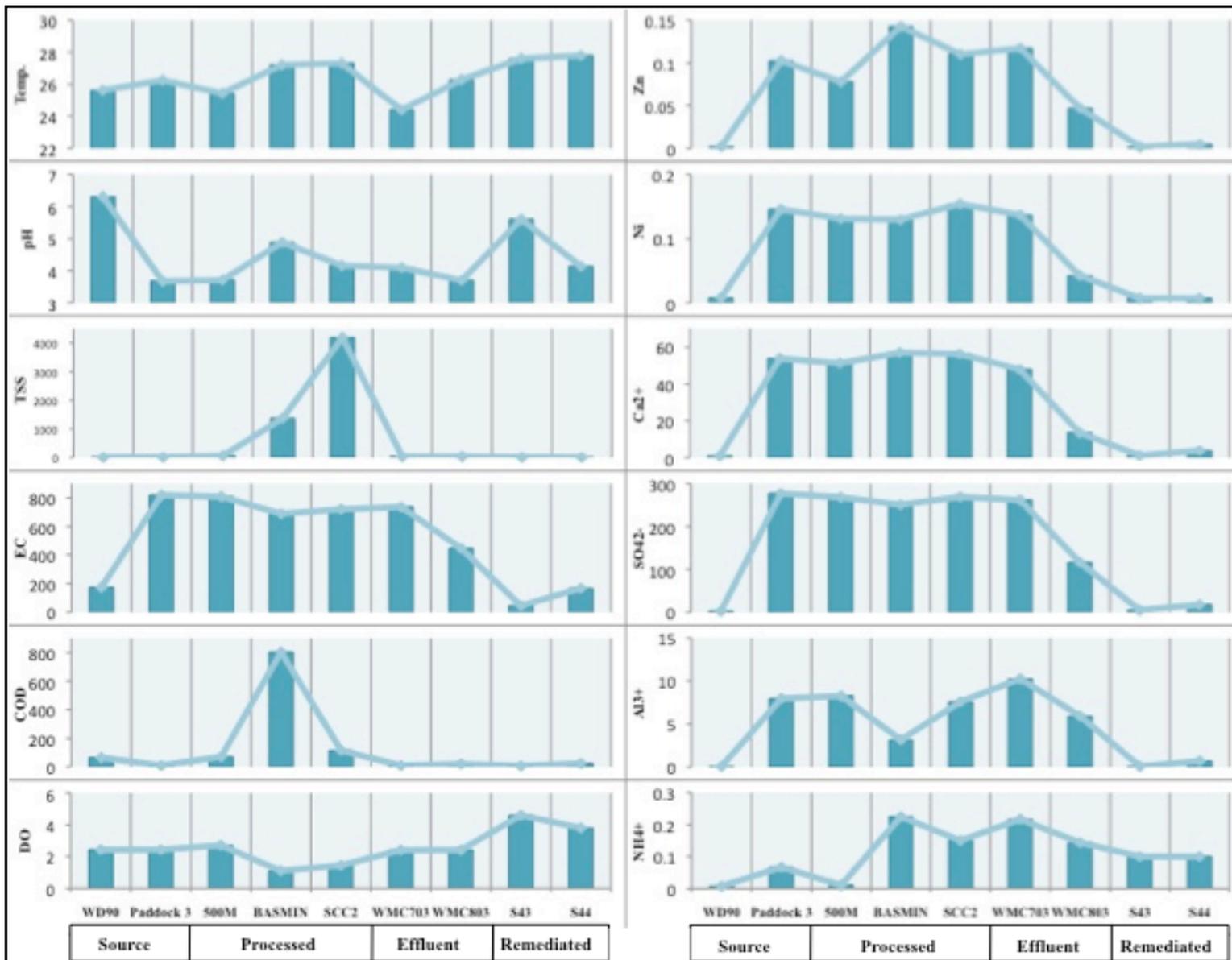


Figure 5: Water quality data for various parameters from April 2013 at each sampling location. The graphs highlight spatial changes in parameters as water moves from the sources (WD90, Paddock 3), to sites on the mine (500M, Basmin, SCC2), to release points (WMC703, WMC803), to discharge points into the MMM River. The flow of water generally progresses east to west. WD90 is the Meandre River source water and Paddock 3 is water recycled by the mine.

Since the start of monitoring for BASMIN and SCC2 in December 2010, average monthly pH values have fallen within QMM established limits (Figure 8). Nearly all pH values are more acidic than the circumneutral pH standard for Madagascar surface waters. Values of the pH are not available for source water points until October 2012; however, available data shows circumneutral pH of source water relative to processed water.

Water used onsite for soaking heavy mineral sands (BASMIN) and for mineral separation (500M) is weakly acidic (pH = 3.56 – 5.60). Effluent water at QMM release points is generally more acidic than processed water (pH = 3.25 – 5.05). Remediated water pH values fall within a range closer to that of the source water (pH = 4.2 – 6.62). The pH trends at Mandena show a lower acidity relative to the extremely conditions (pH often < 2) characteristic of acid drainage associated with metal extraction or natural pyrite oxidation, but the fluids impacted by heavy mineral sand mining are more acidic than pristine river systems (Nordstrom et al. 2011; Sheoran & Sheoran 2006).

Dissolved oxygen values vary greatly from the target DO surface water value of 5 mg/L, spanning a range from 0.26 mg/L to 7.99 mg/L (Figure 9). In general, processed water from the dredging pond has the lowest DO values (DO = 0.26 mg/L – 5.39 mg/L) and remediated water has the highest DO values (DO = 1.67 mg/L – 6.76 mg/L). Deviation from target DO values for all sites appears to decrease with time, beginning in 2012. Data for source water sites is limited, dating back to October 2012.

Consistent analyses of field samples for electrical conductivity (EC) did not begin until 2011. Results since this time show a clear difference between EC values for discharged water, processed water, and remediated water (Figure 10). Processed water and discharged water values lie above the QMM target value of 350 μ S/cm for nearly every month since 2011. Despite several

peaks above the QMM threshold, remediated water in the MMM River falls below the 200 μ S/cm EC threshold for surface water. There is a difference in EC of \sim 600 μ S/cm between the two source waters, Méandre River and Paddock 3.

Sulfate concentrations remain relatively stable over time for each site (Figure 11), with only several months showing abnormally high concentrations (January and October 2012). For every month since operations began, the sulfate concentration for source water and remediated water remained below the 250 mg/L concentration target shared by QMM and the Madagascar government, ranging between 0 mg/L and 136 mg/L. There is an abnormal increase in sulfate concentration at the onsite and effluent release sites between September and October 2012, with a maximum difference of 734 mg/L at the BASMIN site.

Aluminum concentrations are highly variable for both processed water samples ($[Al^{3+}]$ 0.03 mg/L – 8.85 mg/L) and for effluent water samples ($[Al^{3+}]$ 1.06 mg/L – 8.31 mg/L). Al^{3+} concentrations remain low for Méandre River source water and remediated water, reaching a maximum of 0.6 mg/L and 0.5 mg/L, respectively (Figure 12). Lab results for $[Al^{3+}]$ are limited, with monthly analyses beginning in November 2011 and continuing until September 2012, followed by a four-month data gap. There is a steady increase in $[Al^{3+}]$ of processed waters, 500M and BASMIN, throughout the year 2012. $[Al^{3+}]$ results are analyzed with caution because measurements of dissolved aluminum concentration may include contributions from Al-bearing colloids that pass through the filter. It is well established that as filter pore size increases the measured dissolved aluminum concentrations increase as well, skewing results (Rezania 1985). However, aluminum solubility is dependent on pH levels. As the pH decreases the solubility of Al^{3+} increases which could be a cause of the observed increase in $[Al^{3+}]$ (Girard 2014).

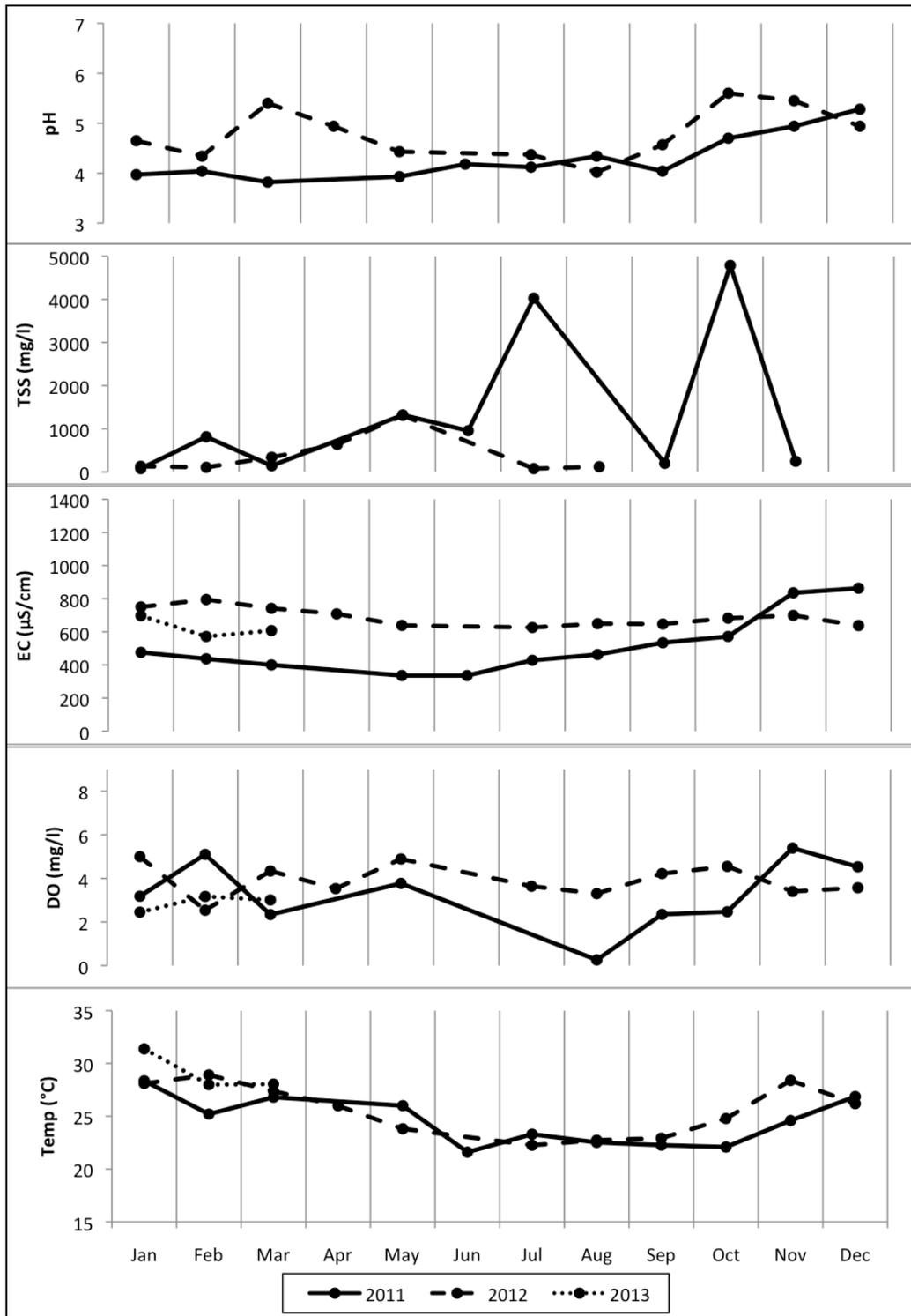


Figure 6 Annual variations of water quality in the mine's dredging basin (BASMIN). Data was not available for pH or total suspended solids (TSS) for the year 2013. Smooth slopes between months delineate missing data.

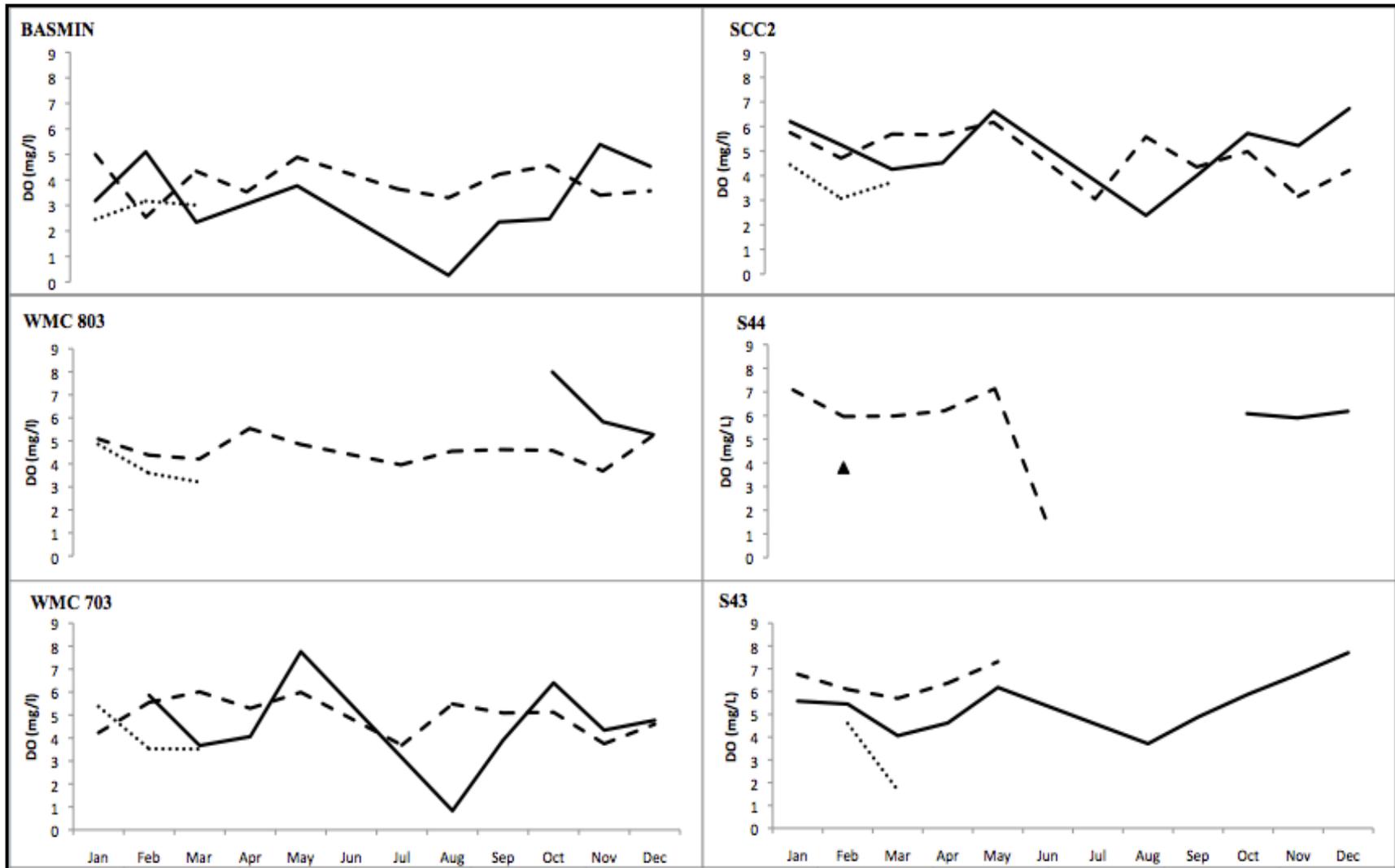


Figure 7 Annual variations in dissolved oxygen content of process water from the dredging pond (BASMIN), canal control point (SCC2), the old effluent discharge point (WMC 703) and its drainage point into the MMM River (S43), and new effluent discharge point (WMC 803) and its drainage point into the MMM River (S44). Limited data was available for source water locations (WD90 and Paddock 3). Solid line represents 2011 data. Dashed line represents 2012 data. Dotted line and triangle in the S44 graph represent 2013 data.

6. DISCUSSION

6.1. Analysis of Spatial Changes in Water Quality

Changes in water quality at each sample site reveal a pattern of deteriorating water quality relative to the control site (WD90), mildly improved quality following treatment in the collector canal, and further improvement in quality after water is naturally remediated in surrounding wetlands (Figure 5). This spatial pattern only explicitly applies for the period of data collection and analyses conducted during April 2013, and should not be considered an all-encompassing pattern for processed water at QMM. In the future, spatial analyses could incorporate hydrological data from the QMM database to compare spatial trends seasonally and/or annually.

A Pearson correlation matrix (Table 2) highlights the physiochemical parameters with strong covariance. Several hydrochemical relationships can be inferred based upon the correlation matrix. High and positive correlation is observed between EC, sulfate, zinc, aluminum, nickel, and calcium ($0.74 < r < 0.99$). There is a high, negative correlation between DO and EC, sulfate, calcium, and nickel ($-0.73 < r < -0.68$). In a well-aerated hydrologic system, DO negatively correlates with WT and EC, due to the dependence of oxygen solubility on temperature and salinity. As water temperature and salinity increase, the solubility of oxygen decreases (Girard 2014). The lack of covariance between WT and DO ($r = 0.23$) reflects the undersaturation of oxygen ($\text{DO} = 1.10 - 4.6 \text{ mg/L}$). The observed DO values are much lower than those of natural conditions ($7.95 \text{ mg/L} < \text{DO} < 8.4 \text{ mg/L}$) corresponding to the observed temperature range ($^{\circ}\text{C} = 24.39 - 27.80$) (Tromans 1998, Appendix B).

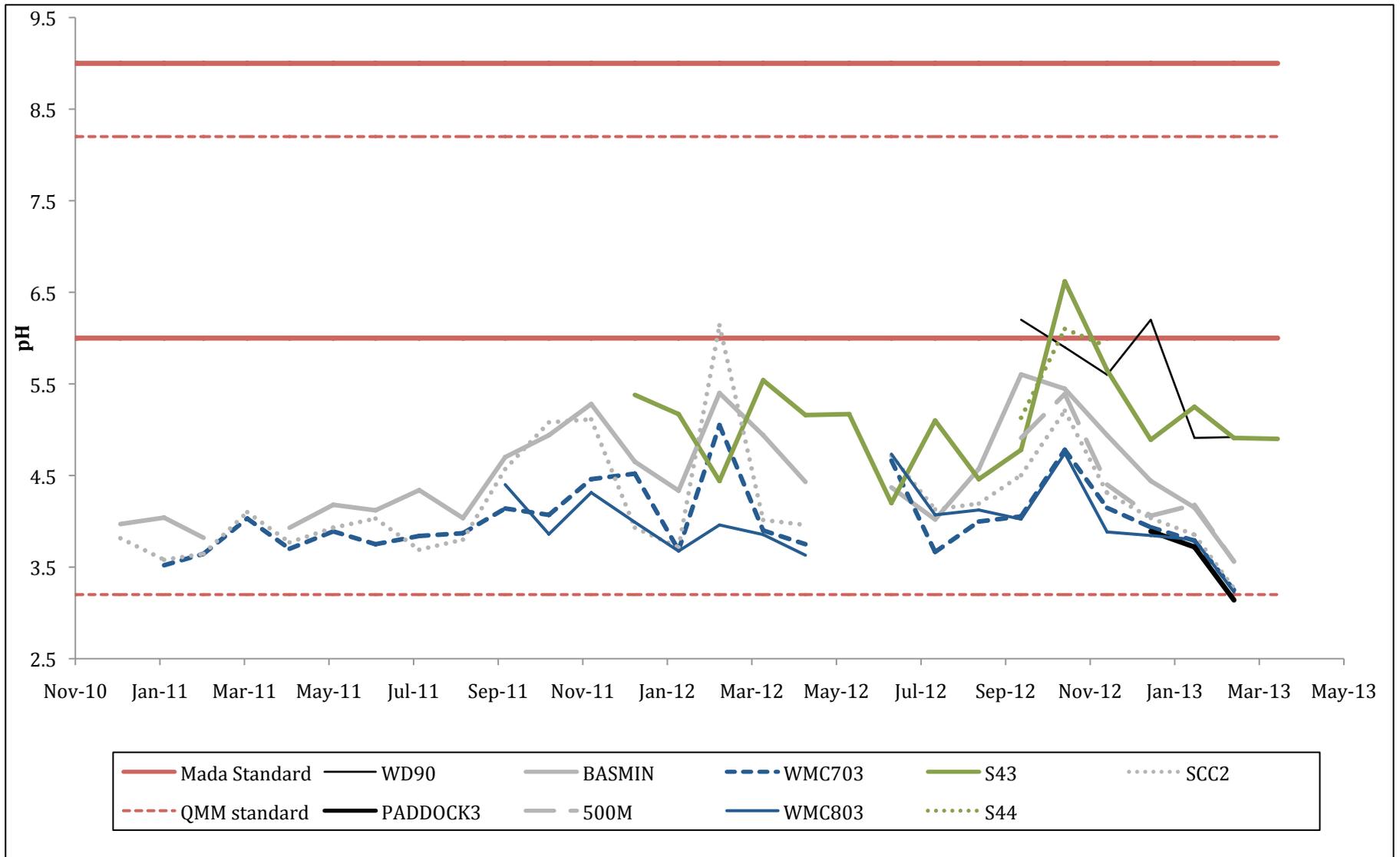


Figure 8 Average monthly pH values for each sampling site. Solid red lines represent the pH range (pH = 6 - 9) for effluent discharge as made law by the State of Madagascar. Dashed red lines represent the pH standards QMM follows, as approved by the State of Madagascar. Notice the significant range of pH that QMM discharge can fall under. Paddock 3 is a new sampling site as of 2013. Paddock 3 is the onsite recycled source water and WD90 is the Meandre River source water.

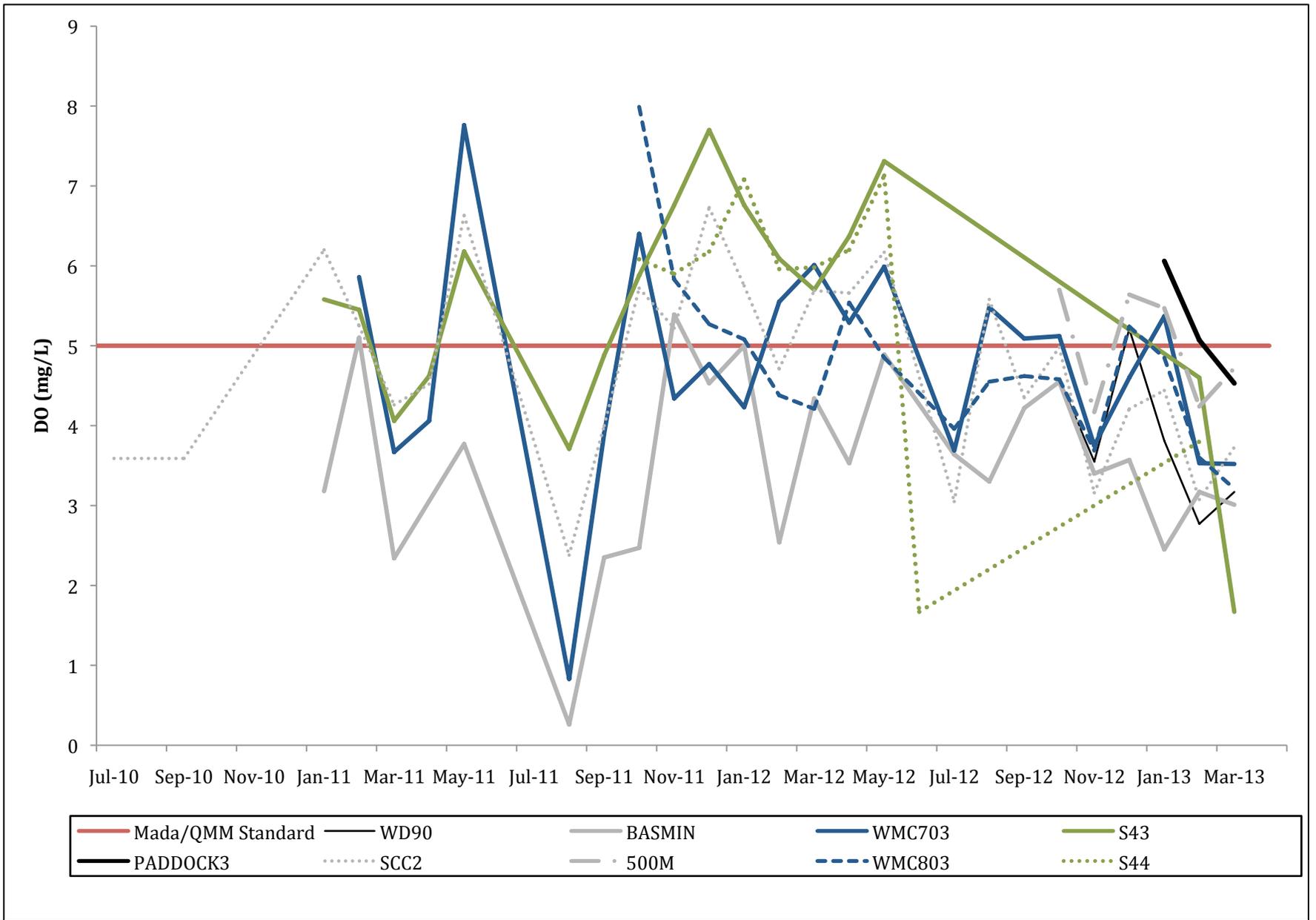


Figure 9 Average monthly dissolved oxygen values for each sampling site. Solid red line represents the State of Madagascar-QMM shared DO limit ($DO \geq 5$) for effluent discharge. Paddock 3 is the onsite recycled source water and WD90 is the Meandre River source water.

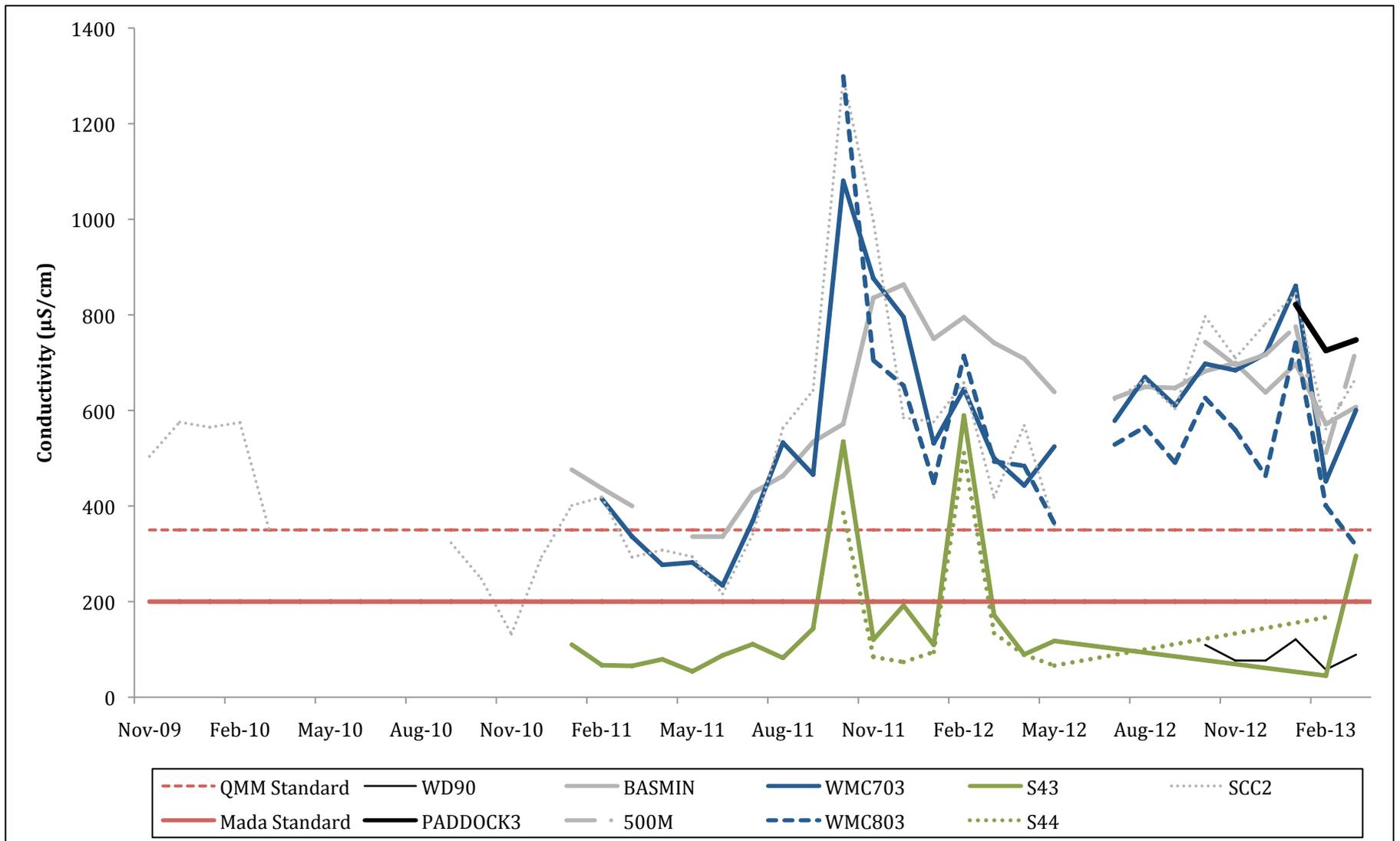


Figure 10 Average monthly conductivity values for each sampling site. Solid red line represents the electrical conductivity limit ($EC \leq 200$) established by the State of Madagascar for effluent discharge. Dashed red line represents the electrical conductivity target value for QMM ($EC \leq 250$) for effluent discharge. Paddock 3 is the onsite recycled source water and WD90 is the Meandre River source water, explaining the distinct difference in the conductivity of these two source waters.

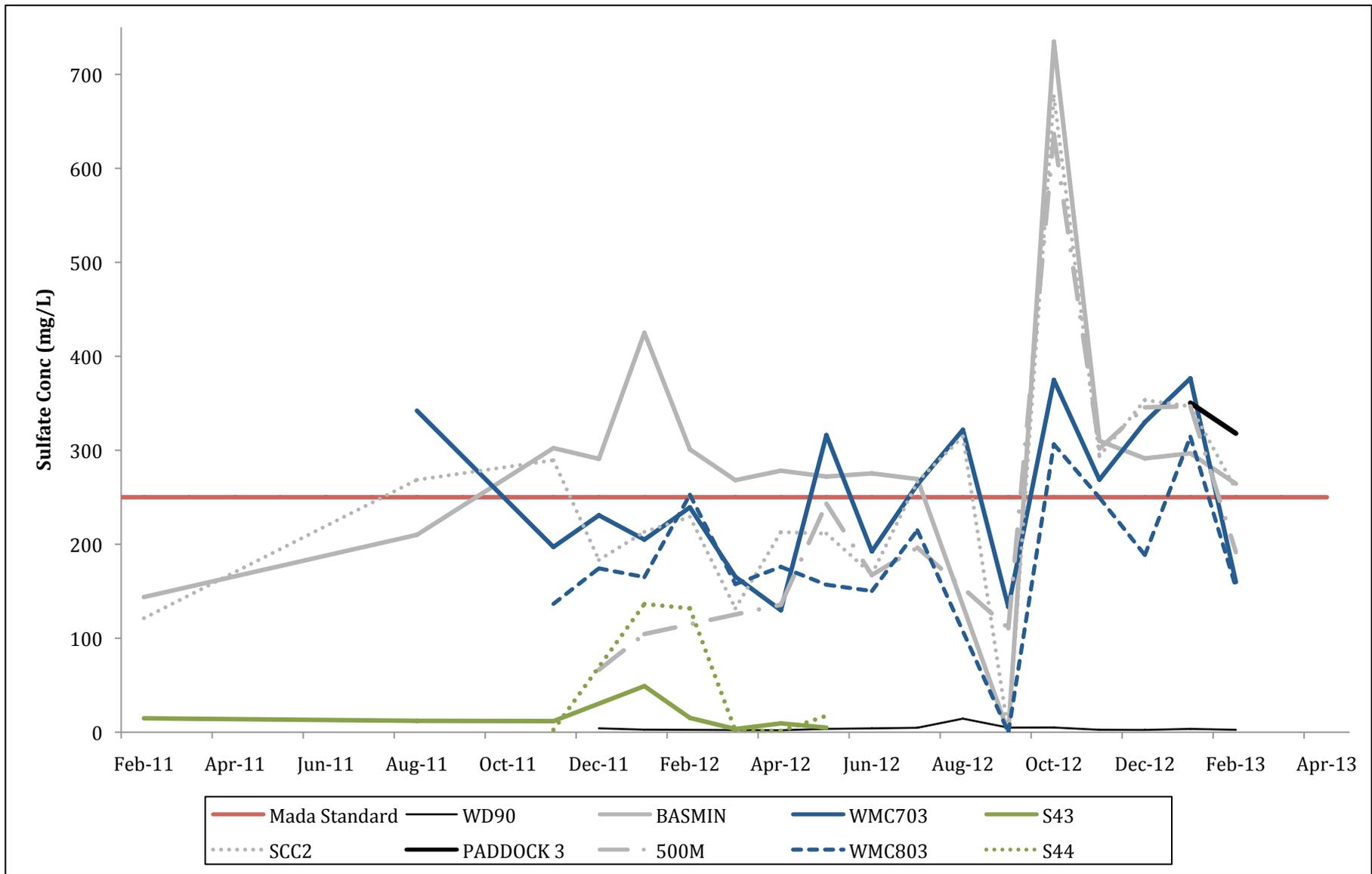


Figure 11 Average monthly sulfate concentrations for each sampling site. Solid red line represents the State of Madagascar-QMM shared sulfate limit ($\text{SO}_4^{2-} \leq 5$) for effluent discharge. Paddock 3 is the onsite recycled source water and WD90 is the Meandre River source water.

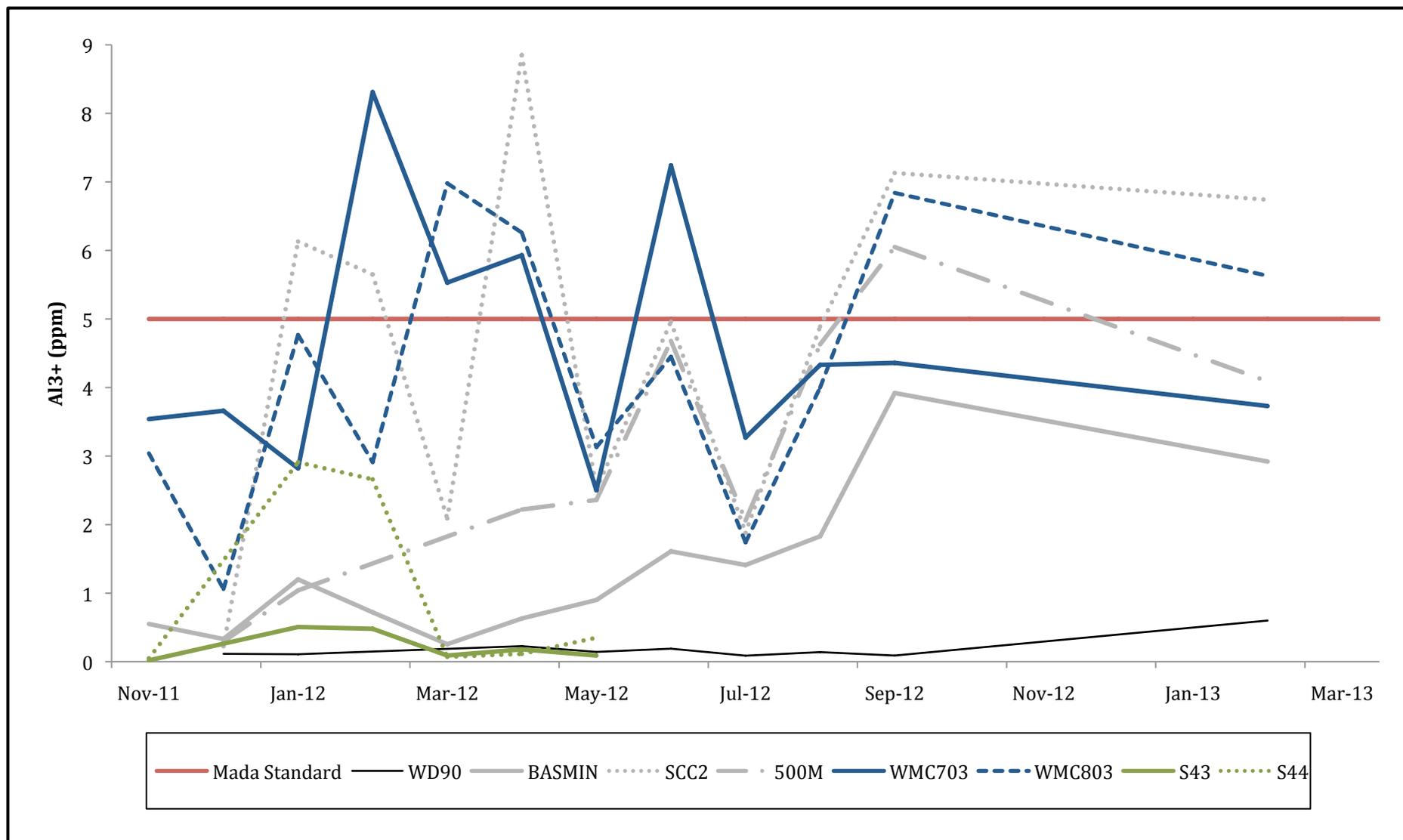


Figure 12 Average monthly aluminum concentrations for each sampling site. Solid red line represents the State of Madagascar-QMM shared aluminum limit ($Al^{3+} \leq 5$) for effluent discharge. Paddock 3 is the onsite recycled source water and WD90 is the Meandre River source water.

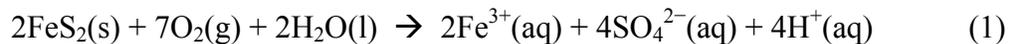
The pH of a solution is arguably the most important factor influencing weakly soluble ionic compounds and the mobilization of trace metals in solution (Girard 2014). From the correlation matrix, pH is negatively correlated to aluminum, salinity, and zinc ($-0.77 < r < -0.67$), and negatively correlated with sulfate, nickel, and calcium ($-0.63 < r < -0.50$). This correlation reflects the oxidation of reduced sediments as the mining pit is dredged and buried sands are exposed at the surface, which lowers pH and increases concentration of sulfates and other dissolved constituents. In all cases comparing pH to dissolved ions, the concentration of dissolved ions increases, and consequently EC, as pH decreases (Figure 14).

High positive correlation between $[Al^{3+}]$ and $[SO_4^{2-}]$ ($r = 0.79$), in conjunction with the lowering of pH, could reflect a geochemical relationship similar to that seen at other acidic sand mining pit lake sites. When exposed to acidic waters ($pH < 4.3$), the iron- and aluminum-rich lateritic clays of this region release dissolved iron and aluminum compounds. In sand pit mining analogues, dissolved aluminum species resulted in precipitation of aluminum-sulfate salts and hydroxyaluminosilicates when exposed to acidic water in the pit lakes and/or the groundwater (Marques et al. 2011). Aluminum is typically hydrolyzed circa pH 5 and removed by mineral precipitation from pH 4 - 5.5 (Nordstrom et al. 2011). Aluminum-bearing minerals may be precipitating, but this cannot be assessed quantitatively without a more encompassing data set of ion concentrations.

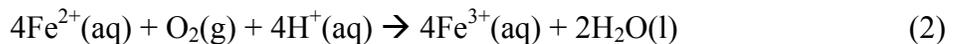
There is a high correlation between Ni and SO_4^{2-} ($r = 0.99$), and both species are highly anti-correlated with pH. As pH decreases, sulfate concentration increases and nickel concentrations increase as minerals containing Ni are dissolved (primarily Ni^{2+}). Nickel could source from limonite-type laterites, which are secondary minerals formed from ilmenite alteration or as a precipitate of iron-bearing solutions, nickel sulfides, or manganese oxides.

Limonite minerals have been recorded at the Ranobe heavy mineral deposit in southwestern Madagascar (Reyneke et al. 2007).

One of the most enlightening ion concentration comparisons is that between Ca^{2+} and SO_4^{2-} (Figure 13). Anhydrite (CaSO_4), or more commonly the hydrated form gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), is found in regional deposits of southeast Madagascar (Morteani et al. 2013). The mass ratio of sulfate to calcium in gypsum is $\sim 2.4:1$; however, the ratio of sulfate to calcium at QMM is $4.5:1$. Excess sulfate, plus low pH, suggests iron sulfide oxidation is occurring. As sands are dredged and separated, sulfides could be oxidized to sulfates, releasing protons and increasing the acidity of the processed water. For example, if the mineral were an iron-sulfide, such as pyrite, it would oxidize as follows:



The oxidation of sulfide to sulfate solubilizes ferrous iron, which could subsequently precipitate out from the oxidized iron as ferrihydrite or oxidize to ferric iron via the following reaction:



After this reaction, the ferric iron could oxidize more pyrite. An additional indication for the presence of an alternative sulfide source stems from the fact that sulfide is dense and would settle out in a placer deposit scenario. Similar oxidation reactions could occur for a variety of sulfide minerals, leading to increasingly acidic wastewaters and release of metals into the environment. Increase in trace metal concentrations could be a result of sulfide mineral sources or increased acidity. The observed aluminum concentrations are likely liberated by the acidity of the processed and effluent waters.

The source of trace metals is dependent on the placer deposit composition. The enrichment of sulfate suggests there is a sulfur source in addition to gypsum present in the sands surrounding Mandena. Considering the decrease in pH and the increase in soluble metals in processed water, the other sulfur source could be detrital sulfides. The increase in aluminum, nickel, and zinc implies that oxidizing minerals could include iron and aluminum rich laterites, nickel sulfides, and zinc sulfides from the weathering of local metamorphic facies.

In addition to revealing the mineralogical characteristics of the mine site, the correlation matrix exposes a set of pronounced water types. The relationships Al v. SO_4^{2-} , Ni v. SO_4^{2-} , and Ca v. SO_4^{2-} exhibit two distinct groups of water, with low- and high- concentrations of dissolved constituents (Figure 14). The distinctness of the two groups (i.e. wide gap in average concentration value) and the fact that few points fall between the two water types, indicate a lack of mixing. The characteristics distinguishing water types are determined using agglomerative hierarchical clustering (AHC).

The division of water types into clusters, based upon statistical similarities of water quality parameters at each sampling site, reflects spatial variance within the Mandena hydrological system (Figure 15). The AHC of QMM sampling sites is very convincing, as the sites within each cluster share similar hydrogeochemical features, as influenced by water usage at different stages of the mining process. In addition, clustering is consistent with the distinctness of water types observed in parameter correlation comparisons (Figure 14). AHC reduced the sampling sites into four classifications of water at QMM, in which cluster 1 (C1) are sites sharing characteristics most similar to natural waters of southeastern Madagascar, cluster 2 (C2) reflecting processed and effluent water types, cluster 3 (C3) distinguished by degraded water quality, and cluster 4 (C4) consisting only of MMM River discharge point S43. The cluster

divisions are reflective of the aforementioned division into source, processed, effluent, and remediated waters, and more specifically, division into either *natural* (source, remediated) or *polluted* (processed, effluent) waters. The level of dissimilarity between clusters further delineates the relative differences of quality between various water types.

The Meandre River source water site WD90 and the MMM release point S44 make up C1. With circumneutral pH values ($5.6 < \text{pH} < 6.3$), EC values less than 200 μm , and low levels of dissolved species, the two sites have geochemical properties comparable to a healthy watershed system (Figure 15; Appendix B). Besides C4, which consists only of MMM River release point S43, C1 has the least within-cluster variance (Appendix E). The shared geochemical characteristics between WD90 and S44 could be a reflection of across-watershed similarity in water composition and/or the natural remediation of effluent as it migrates through the estuarine tributary before release into the MMM river. Although there is little dissimilarity between C1 and C4, there are hydrochemical differences between the two that explain the distinction. C4 has higher salinity, lower pH, EC, COD, and concentration of dissolved constituents. The salinity difference ($C1 = 0.08 \text{ psu}$, $C4 = 0.303 \text{ psu}$) is most likely a result of the closer proximity of S43 to the ocean and the potential for freshwater-saltwater mixing (Figure 3). An attenuation effect, as discharged water flows downstream from S44 to S43, could be the cause for further natural remediation and a lower concentration of dissolved constituents (Odor et al. 1998). Despite slight dissimilarity between C1 and C4, the water quality characteristics are essentially the same, and together sites within these clusters are considered reflective of ‘natural waters.’

C2 consists of effluent discharge sites WMC703 and WMC803, recycled source water site PADDOCK 3, and MSP discharge site 500M. WMC703 was the class centroid (i.e. the

Euclidean distance reference value minimizing within-class variance) for the AHC analysis of C2 (Appendix E). Relative to other clusters, C2 represents waters with the lowest pH values and highest salinity and EC values. Within the cluster, PADDOCK 3-WMC 703 and 500M-WMC803 are paired based on similarity in water composition, reflecting simply the flow pattern of water across the mine (Figure 3).

The inclusion of both effluent and processed waters in C2 was surprising, considering the effort by the mine to remediate processed water before release into the environment. Because of the mixing of water with heavy mineral sands at the MSP, water composition of 500M discharge was hypothesized to be more closely related to waters in the dredging pond, BASMIN. If remediation were completely effective, a greater dissimilarity between processed waters (500M, PADDOCK 3) and effluent (WMC703, WMC803) would be expected. Although both C2 and C3 contain sites degraded in quality relative to natural waters, the way in which the water quality is poor is different. High TSS and turbidity, greater than all other clusters by two orders of magnitude, characterize C3 sites BASMIN and SCC2 (Appendix B). The dissolved constituent concentrations, however, are comparable to those of C2. Al and Zn concentrations are higher in C2 (8.5 and 0.9, respectively), whereas, SO_4^{2-} , Ca, and Ni are higher in C3 (259.8, 61.1, and 0.14, respectively). The disparity between C2 and C3 indicate that the physical remediation process by the mine allows for effective removal of TSS and turbidity from the water column, but is not efficient in remediating dissolved constituents.

There is a clear distinction between ‘natural’ (C1, C4) and ‘polluted’ (C2, C3) waters at Mandena. Spatial differences in water quality, emphasized by multivariate statistics, exhibit that more remediation is occurring by natural remediation processes, then by onsite improvement

strategies. Not until effluent flows through the estuarine system surrounding the mine, is effluent remediated to a level comparable to its original composition.

6.2. Analysis of Temporal Changes in Water Quality

Temporal trends highlight the effect of seasonality on water quality parameters, the gaps in data, and the effectiveness of water management based on variance from established water quality criteria. Temperature trends in the annual comparisons exhibit the seasonal transition from warm, dry, summer months (November to May) to cold, wet, winter months (June to October). Seasonal changes in precipitation and temperature are important aspects of water quality to consider due to their influence on other physiochemical parameters.

Seasonal rainfall events could influence the magnitude of impact on the environment by mining effluent in three ways: tidal infiltration, spillover effect, or flushing. The coastal river systems in Fort Dauphin are subject to tidal movement at low elevations, and consequently affected by saline dispersion and diffusion. Tides can infiltrate up to 5 km into the MMM River catchment, which is hydraulically connected to the Mandena aquifer (Vincelette et al. 2007). Extreme peaks in salinity data could be a result of saltwater mixing with the MMM Catchment during the rainy season, while EC/salinity peaks during dry periods are indicative of evapoconcentration (Marques et al. 2012). In the case of extreme rainfall events, processed water can breach the collector canal banks and spill over into the marsh habitats surrounding Mandena (Pers. Comm. Bemana).

Another control on water quality parameters is flushing by early-season storms. The first storms of the rainy season tend to result in a sharp spike in dissolved ions, due to initial catchment flushing of concentrated constituents throughout the dry season (Marques et al. 2011). Specifically, water table lowering during the dry season is conducive to increased sulfide

oxidation, producing sulfates that are later mobilized during the first rainfall event (Ohimain 2011).

Both the annual and monthly temporal comparisons provide a good visualization of gaps in the water department's hydrology database. The disclosure of data gaps reveals how the QMM water management plan has evolved over time by showing when particular parameters or sampling locales were added. More importantly, the data gaps reveal the inconsistency of sampling and analysis. For example, the canal control pond (SCC2) has been monitored the longest (beginning in January 2009), while BASMIN and SCC2 have been sampled the most frequently. Measurements of conductivity began the earliest (November 2009), but sampling of pH at each site has been the most consistent. On the other hand, many important hydrological parameters, such as turbidity and trace metals, were not evaluated consistently in the field or the lab until 2012.

The most challenging aspect of the data gap stems from the lack of water quality data for the control site (WD90), which has only been sampled since October 2012, and the remediated sites (S43 and S44), which have only been sampled since January 2011. Without data for a control site representing a regional, healthy hydrologic system, it is difficult to conclude how effluent quality has changed and the potential impact of these changes on the environment. The lack of data for the remediated water sites before 2011 makes it difficult to gage if discharged water was remediated to an appropriate level during this period, or if water management at QMM has improved.

	WT	pH	Sal.	EC	TSS	Turb.	DO	COD	SO ₄ ²⁻	Ca ²⁺	Al ³⁺	Ni	Zn	NH ₄ ⁺
WT	1.00													
pH	0.14	1.00												
Sal.	0.04	-0.67	1.00											
EC	-0.43	-0.66	0.66	1.00										
TSS	0.36	-0.08	0.21	0.33	1.00									
Turb.	0.38	-0.05	0.22	0.35	0.99	1.00								
DO	0.23	0.19	-0.06	-0.70	-0.57	-0.63	1.00							
COD	0.26	0.17	0.09	0.25	0.30	0.45	-0.59	1.00						
SO ₄ ²⁻	-0.36	-0.63	0.72	0.99	0.40	0.43	-0.68	0.30	1.00					
Ca ²⁺	-0.27	-0.50	0.70	0.94	0.51	0.56	-0.73	0.44	0.97	1.00				
Al ³⁺	-0.66	-0.77	0.59	0.83	0.01	-0.03	-0.32	-0.27	0.79	0.65	1.00			
Ni	-0.32	-0.56	0.72	0.97	0.47	0.50	-0.69	0.30	0.99	0.98	0.74	1.00		
Zn	-0.58	-0.71	0.66	0.90	0.25	0.22	-0.45	-0.14	0.89	0.81	0.96	0.87	1.00	
NH ₄ ⁺	0.09	-0.09	0.18	0.16	0.35	0.42	-0.35	0.51	0.25	0.37	-0.02	0.24	0.09	1.00

Table 2 Correlation matrix for major ions, water temperature (WT), pH, EC, TSS, salinity with units psu (Sal.), turbidity with units NTU (Turb.), DO, and COD. Bold values indicate significant correlations ($p < 0.05$).

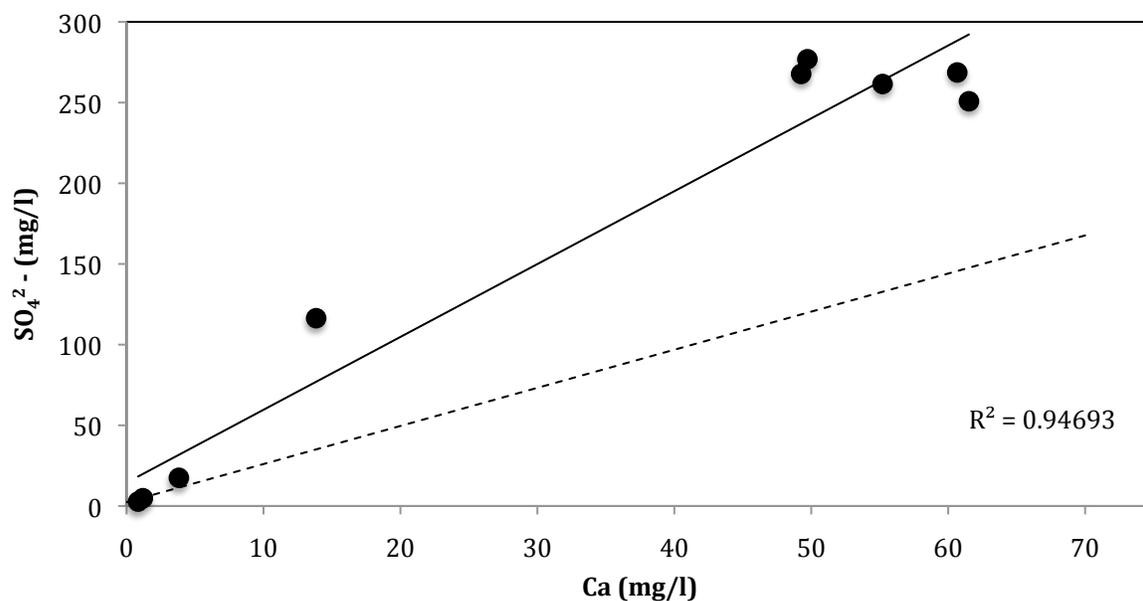


Figure 13 Plot comparing calcium (Ca) and sulfate (SO₄²⁻) concentrations at each sampling site, with the solid line representing the linear regression of these points. The dashed line represents the stoichiometric ratio of Ca and SO₄²⁻ in gypsum (SO₄²⁻/Ca = 2.395).

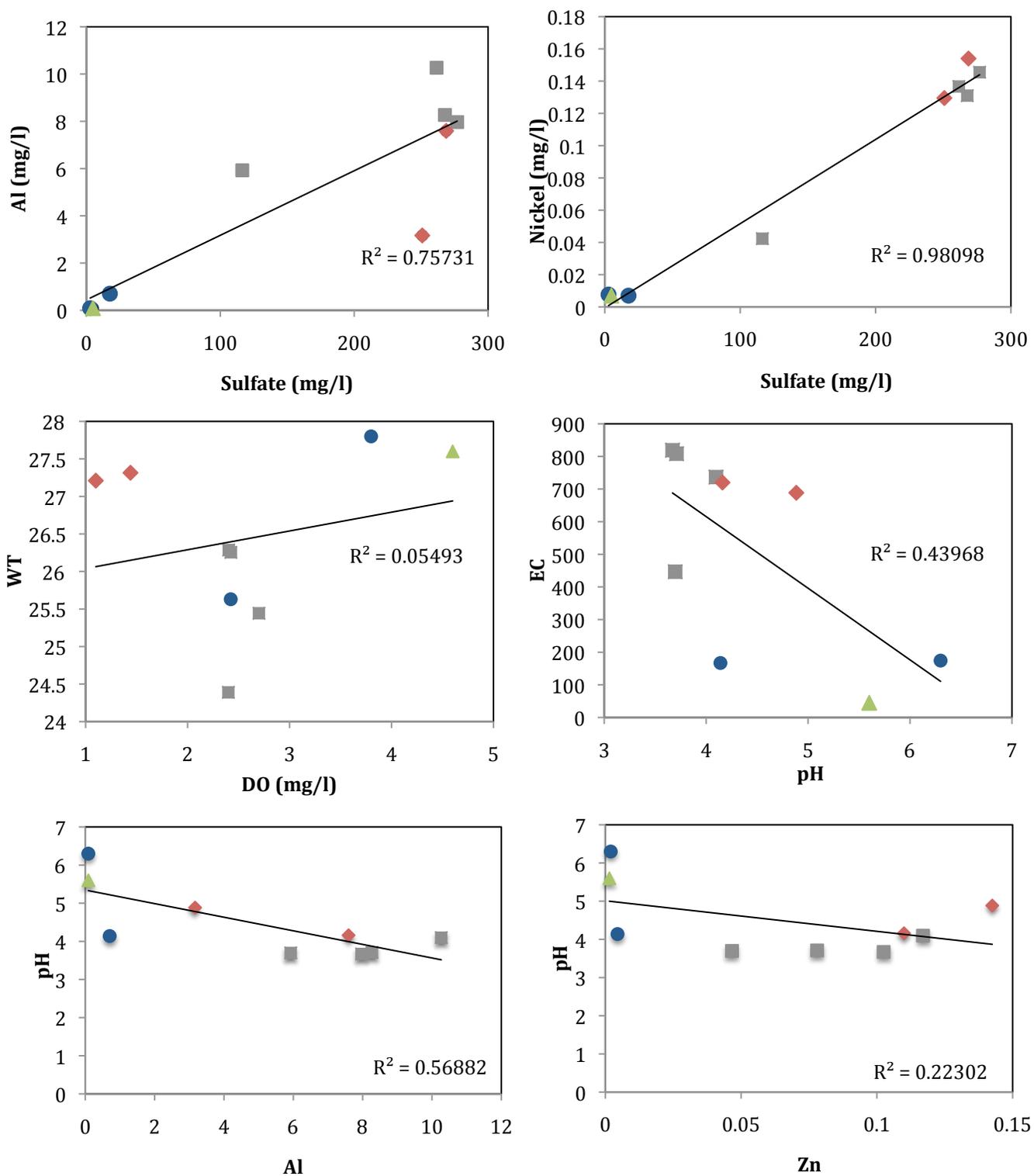


Figure 14 Al v. SO_4^{2-} , Ni v. SO_4^{2-} , DO v. WT, pH v. EC, pH v. Al, pH v. Ni plots for data collected at QMM during April 2013. Data point symbols correspond to sites within clusters. Blue circles represent C1 (WD90, S44), gray squares represent C2 (Paddock 3, WMC703, WMC803, 500M), red diamonds represent C3 (BASMIN, SCC2), and green triangle for C4 (S43).

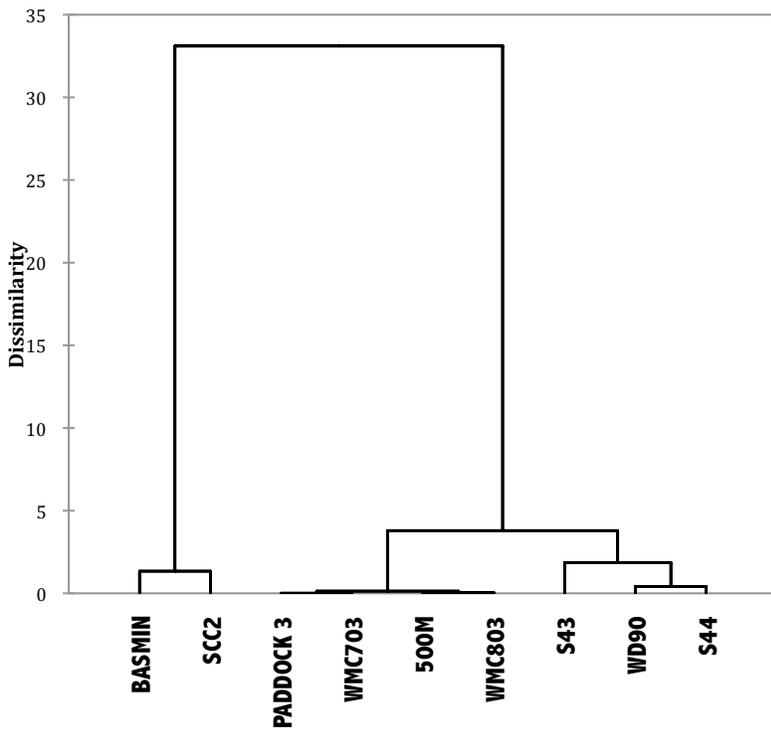
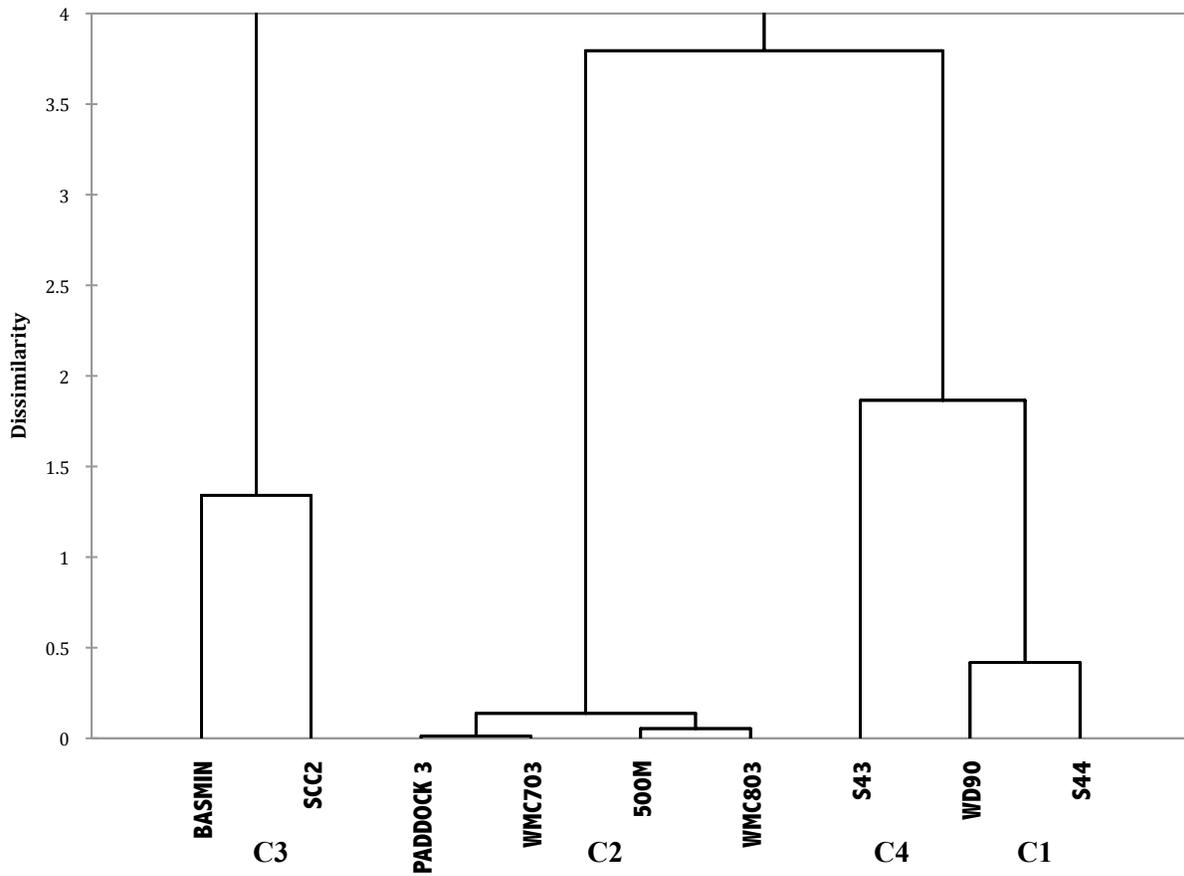


Figure 15 Dendrogram showing agglomerative hierarchical clustering of sampling sites based on similarity in chemical composition during April 2013. Above: enlarged dendrogram highlighting specific values for sampling sites. Left: same dendrogram as above, showing maximum dissimilarity between Cluster 3 (BASMIN, SCC2) and Cluster 4 (S43). Cluster 2 consists of WMC703, WMC803, Paddock 3, and 500M. Cluster 1 consists of S44 and WD90.

	Cluster 1	Cluster 2	Cluster 3	Cluster 4	
	Mean	Mean	Mean	Mean	Std. Dev.
WT	26.72	25.60	27.27	27.60	1.14
pH	5.22	3.80	4.53	5.60	0.93
Salinity	0.19	0.34	0.34	0.30	0.10
EC	170.65	702.67	704.25	45.00	308.70
TSS	3.78	30.07	2783.48	7.13	1408.27
Turbidity	5.24	35.25	2468.00	4.05	1155.97
DO	3.11	2.48	1.27	4.60	1.07
COD	44.00	27.00	459.50	6.00	257.46
SO ₄ ²⁻	10.11	230.64	259.75	4.84	125.79
Ca ²⁺	2.33	42.01	61.09	1.19	27.11
Al ³⁺	0.38	8.45	3.64	0.09	4.10
Ni	0.01	0.11	0.14	0.01	0.07
Zn	0.00	0.09	0.07	0.00	0.05
NH ₄ ⁺	0.06	0.10	0.19	0.10	0.09

Table 3 Mean values for hydrochemical compositions in spatial clusters of sampling sites on and near QMM. Units in mg/L, except for EC ($\mu\text{S}/\text{cm}$), salinity (psu), turbidity (NTU), and water temperature (WT, $^{\circ}\text{C}$). Cluster 1 consists of sites S44 and WD90; Cluster 2 sites WMC703, WMC803, Paddock 3, and 500M; Cluster 3 BASMIN and SCC2; and Cluster 4 site S43.

In addition to monthly and annual analyses, temporal observation of water quality changes can be reduced to an even smaller timescale. Diel biogeochemical processes, controlled by changes in temperature and sunlight exposure over the course of a day, can have a minor effect on hydrochemistry and influence interpretations of water quality data. The dependence of reaction kinetics and equilibria on temperature can affect the solubility of minerals and gases, sorption of metals and metalloids, toxicity of contaminants, kinetics of microbiological metabolic processes, and suitability of wetland environments for aquatic life (Nimick et al. 2011). Diel hydrological factors are addressed by measurement of water temperature during field sampling, but could be considered more explicitly in future analyses.

The comparison of water quality data to national- and company-established criteria offers insight into the effectiveness of processed water treatment and quality monitoring. For example,

pH values at each site meet the established effluent criteria, yet there is a visible difference in pH of the effluent and remediated water. The fact that effluent (WMC703 and WMC803) becomes less acidic when discharged into the MMM River (S43 and S44) could be an indication of natural remediation processes not associated with the QMM treatment process. For other parameters, such as EC and DO, strict adherence to target limits is not followed due to a lack of oversight by the State of Madagascar. Yet the variance in EC and DO is very great, reaching upwards of 1000 $\mu\text{S}/\text{cm}$ and 4.5 mg/L for EC and DO, respectively. The wide variance indicates that water quality may not have been completely treated during several months before discharge into the environment. In general, the temporal analyses provide insight into the effectiveness of the QMM sampling protocol and are important to consider when judging the strengths and weaknesses of QMM water management.

6.3. QMM Water Management and Monitoring Practices

Water management at QMM is an extensive project, requiring management of six different water types: drinking water, domestic wastewater from employee housing, marine water near Port d'Ehoala, surface water, groundwater, and processed water (Pers. Comm. D. Bemana). To ensure protection and appropriate mitigation of potential environmental impacts, including a focus on water-related issues, QMM outlined a Project Environmental Management Plan (PEMP) in 2001. Because hydrological analyses in this study focus solely on processed water, conclusions drawn about water management by the *Service de l'Eau* are only strictly applied to processed water resources, and loosely extended to the overall system of water management.

Adequate monitoring of processed water should include analysis of both the physical and chemical variations in water properties, as well as analysis of these components at different scales, from the molecular level to the watershed level. At the watershed level, deforestation and soil disturbance associated with heavy mineral mining can have an impact on natural runoff and drainage dynamics. To manage the modification of drainage following construction of mining infrastructure (canal, basins, ridges, etc.), the PEMP proposed to develop adequate drainage networks and rehabilitate wetlands to help manage runoff. The reforestation of the littoral forests is an effort to rehabilitate the wetlands to its original state. Another considerable mining effect on the watershed includes modification of water and sedimentary balance characteristics. This in turn has an effect at the ecosystem- and species-level due to the influence of changing water conditions on biology. The PEMP proposed to address this by increasing monitoring during rainy season and by constructing sediment barriers. Finally, increased turbidity was identified in the PEMP as a potential negative hydrological impact. To address this, QMM proposed establishing an adequate drainage network, development of a retention basin, and extensive water quality monitoring. The first two proposed management measures were followed, yet monitoring of turbidity did not begin until 2012.

Incorporating study and monitoring of microbiological and environmental remediation elements within the water management protocol at QMM would foster a better understanding of biological controls on water quality and natural remediation/attenuation processes. Second only to BASMIN, SCC2 had the most elevated levels of TSS during April-May 2013. Extreme levels of TSS can cause significant ecological degradation of aquatic environments. Physically, excessive TSS could reduce penetration of light through the water column, influence temperature, and/or infill channels feeding the MMM River. Chemical alterations caused by TSS involve

release of heavy metal contaminants and nutrients (Bilotta & Brazier 2008). Monitoring at SCC2 of TSS behavior, as well as other chemical and biological quality effects, is one area in which the *Service de l'Eau* can expand its monitoring program to ensure limited effect of mining effluent on the natural hydrological system of Mandena.

Wetland remediation processes, such as dilution and soil filtration, are effective ways by which water quality is remediated (Pound et al. 2013; Sheoran & Sheoran 2006). However, the capacity for river and rainfall dilution of contaminants may be limited as annual precipitation levels are projected to decrease (Snook et al. 2004). This suggests QMM incorporate climate change adaptability into water management decisions.

To rehabilitate the littoral forest stands, mine tailings from the MSP are disposed of in the mined out dredge path and replanted with native seedlings (Dumouchel et al. 2005). Changes in the chemical composition of tailings could thus have an effect on the regrowth process. Littoral deforestation of Mandena as the mine migrates changes the geochemistry of the sands as well, by removing shallow root systems that release organic compounds and alter soil acidity. However, this impact is small in comparison to changes caused by mineralogical controls and sulfide oxidation. Environmental degradation is not solely associated with the water quality of effluent, but also with effects on hydrological dynamics resulting from deforestation. Future evaluation of changes in discharge and drainage patterns caused by the migrating mine system could contribute to understanding the extent of hydrological alteration within the Lanirano and MMM River catchments.

6.3.1. Strengths and Weaknesses

After conducting temporal and spatial hydrologic analyses, QMM requested a critique of the current water management regime at the mine. The strengths and weaknesses of the *Service de l'Eau Déchets* became apparent after following the *Méthode de Travail Normalisée* (MTN) for water quality monitoring, conducting laboratory analyses onsite at QMM, accessing the complete QMM hydrological database, and observing general management practices. Strengths include the *Service de l'Eau's* ability to adapt in response to a migrating mine, capacity to balance time and resources, collection of raw data, and the effectiveness of the collector canal treatment system in remediating turbidity. Weaknesses include the frequency and consistency of field sampling, lack of several lab analyses, time gap between data collection and approval for water release, insufficient graphical and statistical analysis of data, and inadequate dissolved constituent remediation before effluent release.

The nature of the ilmenite mining process requires continuous movement of the mine as the dredge exhausts the quantity of titanium dioxide ores. Due to the migration of the dredging pond, the flow of water resources and the nature of the collector canal also change. Considering this, the *Service de l'Eau* continuously adapts their monitoring protocol, sampling locale, and sampling frequency. Personal observation and participation in MTN methodologies revealed the flexibility of the QMM water management program. Considering the breadth of monitoring requirements, the size of the water management team, and the available hydrological tools, the *Service de l'Eau* also does a good job balancing time amongst many monitoring tasks. Another strength of the *Service de l'Eau* is the quantity of raw data collected. Although there are gaps in processed water sampling, the total amount of raw data collection provides at least a weekly or bi-weekly baseline dataset for each water type monitored by QMM. Finally, the collector canal

and the recycled water cycle at QMM proved effective as a physical water treatment system for colloidal suspension reduction.

Due to a need to balance monitoring of many different water types, sampling at processed water sites is inconsistent and infrequent. The fluctuation of effluent water quality in parameters, such as dissolved oxygen, electrical conductivity, and sulfate, suggest time and resources should be redistributed to improve monitoring of processed water resources. Currently, analysis of microbiological parameters requires shipment of water samples to a lab in Madagascar's capitol, Antananarivo. This delays knowledge of potential effluent quality problems until after effluent is already discharged. The most significant issue with water management at QMM is the lack of graphical and statistical analysis following data collection. Despite a large database of hydrological parameters, limited manipulation of data is conducted to track water quality changes over time or by site. Analysis of water quality data is only completed for annual reports (Pers. Obs.). The deficiency in graphical and statistical analysis prevents the company from tracking progress, monitoring effects on the environment due to effluent quality, and preparing for future management adaptation. The deficiencies in the monitoring protocol at QMM lend to an "appearances-only" approach to water management. In other words, monitoring is completed to comply with corporate environmental regulations, but little is done with the data to encourage preservation of the impacted environment. The financial additive of adding time, labor, and resources into addressing these weaknesses in the water management program, could be viewed by QMM as an investment into company sustainability and resiliency (Sadoff 2009).

7. CONCLUSION

Spatiotemporal hydrologic analyses were a useful tool in the evaluation of the water management regime at QIT Madagascar Minerals, providing insight into the mineralogy of the

region, natural controls on hydrogeochemical properties, and the importance of a comprehensive corporate management of water resources for conservation of a healthy watershed. The Mandena mine site lies on a deposit of lateritic clays and sulfide-bearing minerals, as reflected in the lowering of pH, increase in sulfate concentration, and mobilization of trace metals in processed waters. Source waters are polluted during mining processes, remediated in turbidity and TSS before discharged as effluent, and naturally remediated via soil filtration and dilution processes as effluent migrates through the Mandena wetland environment toward the MMM River.

Water supplies must be continually monitored throughout the process of ilmenite mining to ensure acceptable water quality. Effluent discharge is not holistically remediated, or exhaustively monitored, by QMM before release into the environment. Effective water management is essential for the benefit of the mining company, in that water supplies must remain fresh for the rehabilitation of ore deposits following extraction, and for the environment, in that sustaining natural hydrological processes are necessary to maintain the biodiversity and health of the surrounding ecosystem. Despite several points of weakness in their oversight of effluent hydrogeochemistry, QMM is improving upon their system of water management. The company is currently developing a water balance model to improve monitoring of water flow and installing new laboratory equipment for onsite microbiological analyses. Due to the evolving nature of QMM, frequent assessments should be conducted in the future to track the progress of the water department and the effects of mining effluent on the littoral forest environment. Consideration of water flow dynamics, placer deposit mineralogy, and natural controls on water quality parameters can provide a more comprehensive idea of hydrogeochemical changes to mining waters and consequential impacts to the environment.

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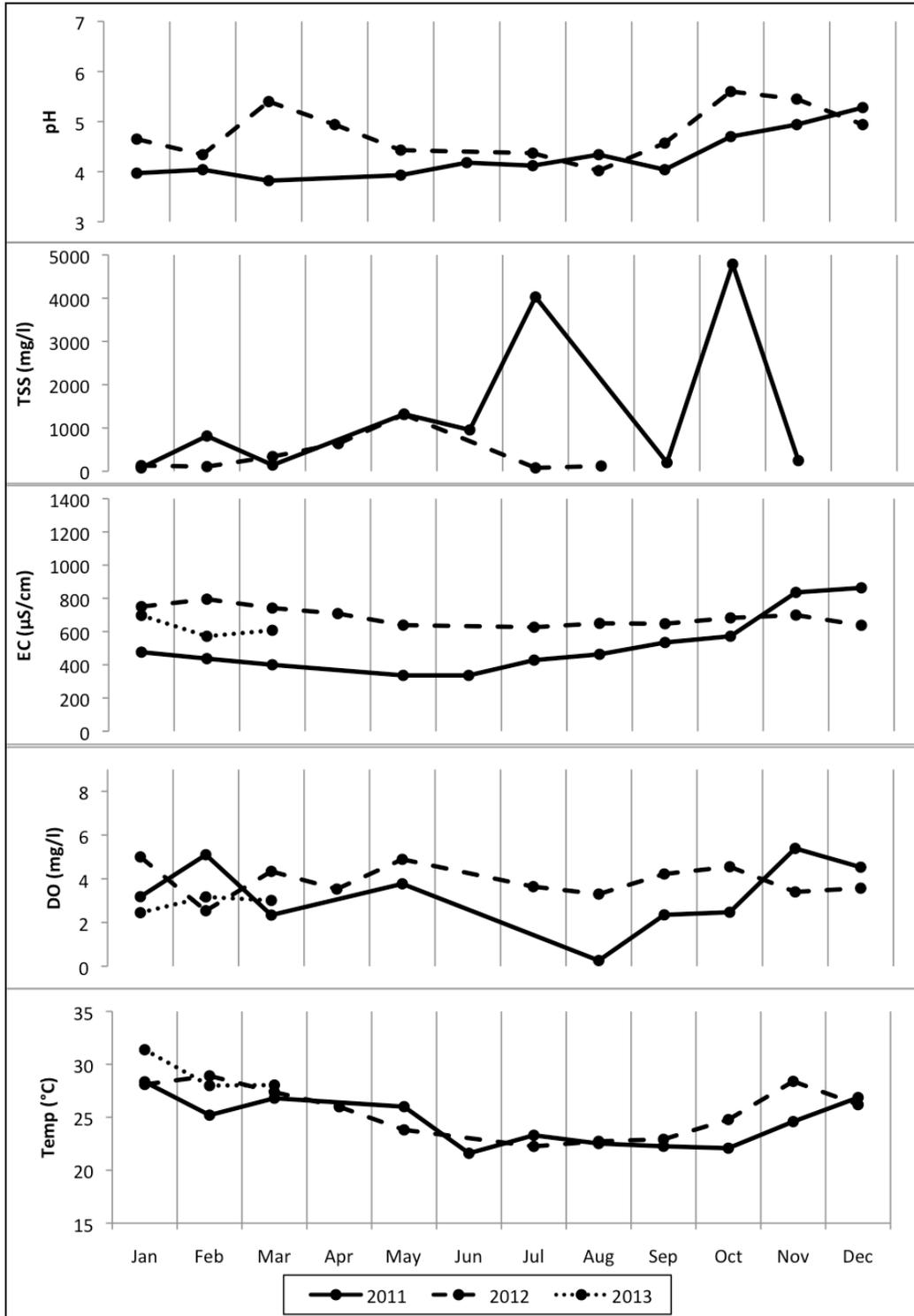
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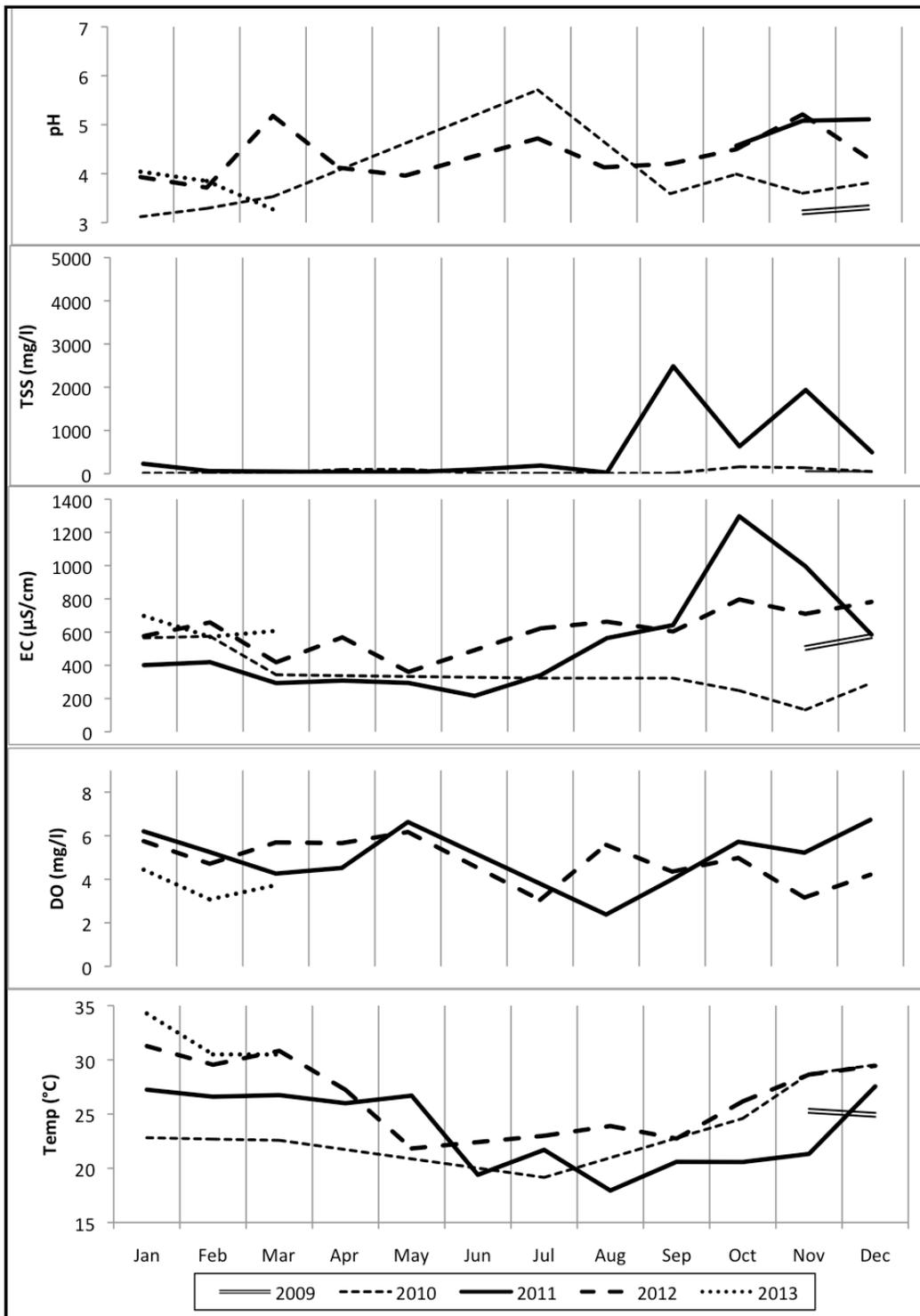
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APPENDIX A:

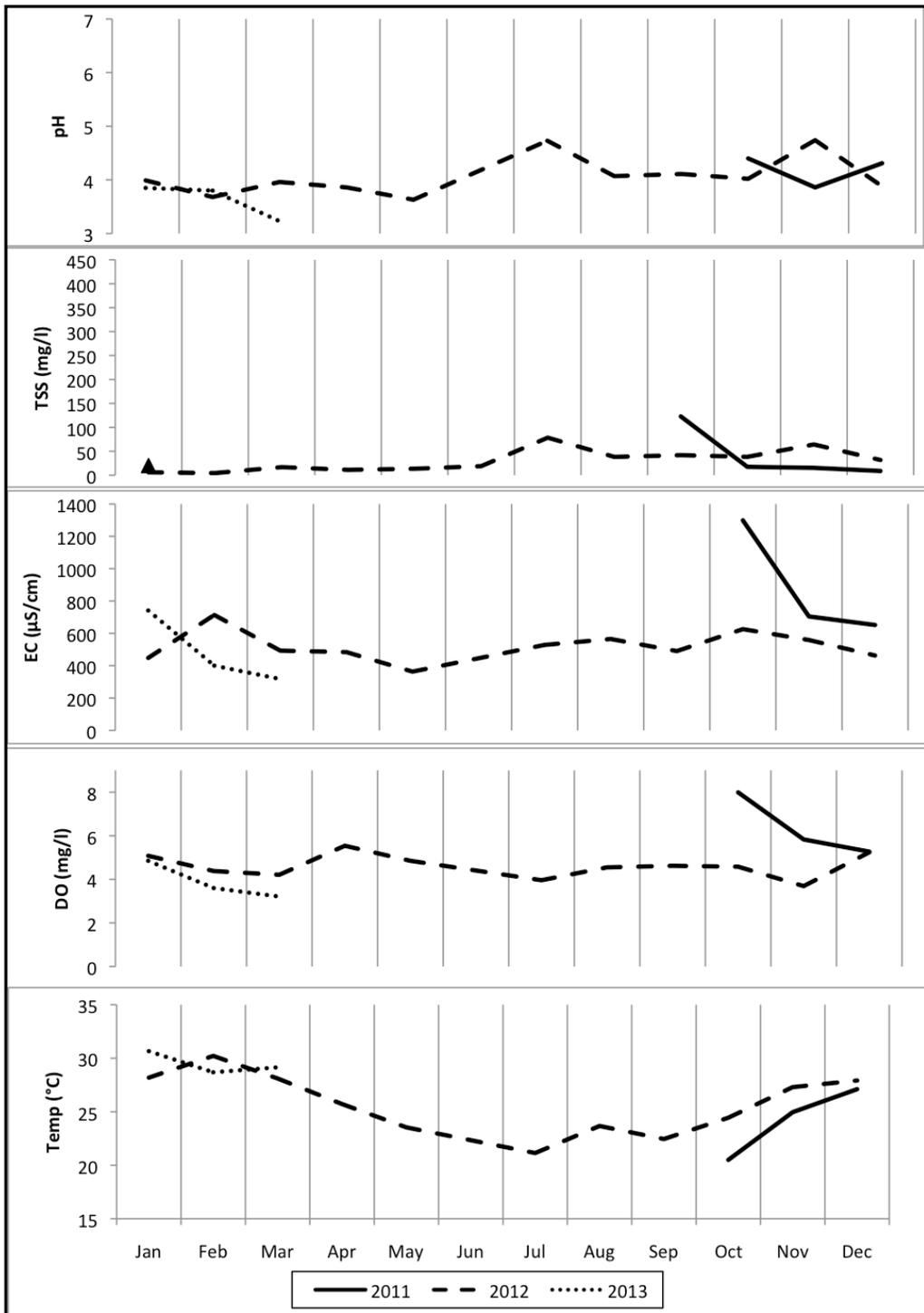
Annual Variation in Processed Water Quality, Graphs for Each Sampling Site



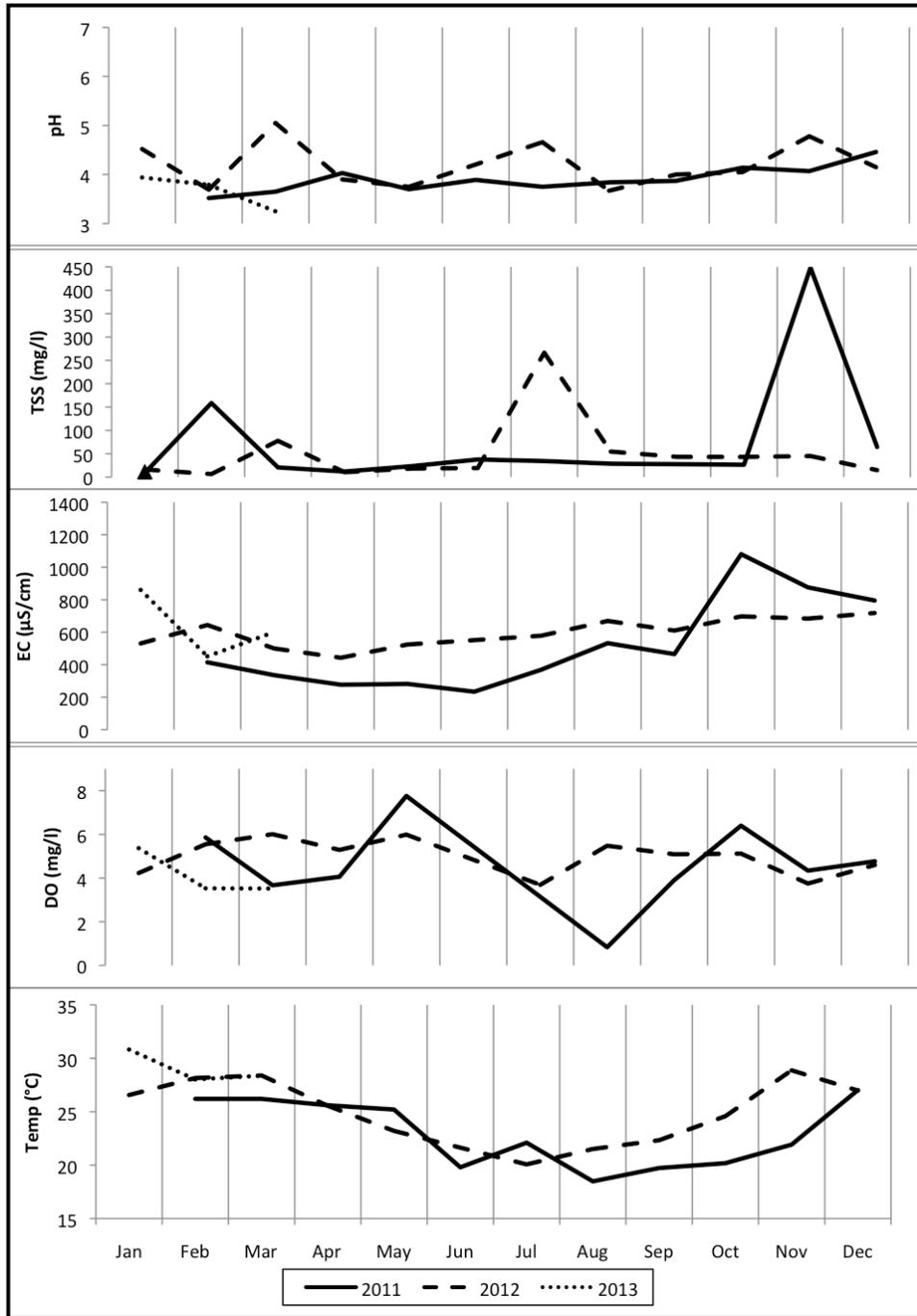
BASMIN Annual variations of water quality in the mine’s dredging basin. Data not available for pH or total suspended solids (TSS) for the year 2013. Smooth slopes between months delineate missing data.



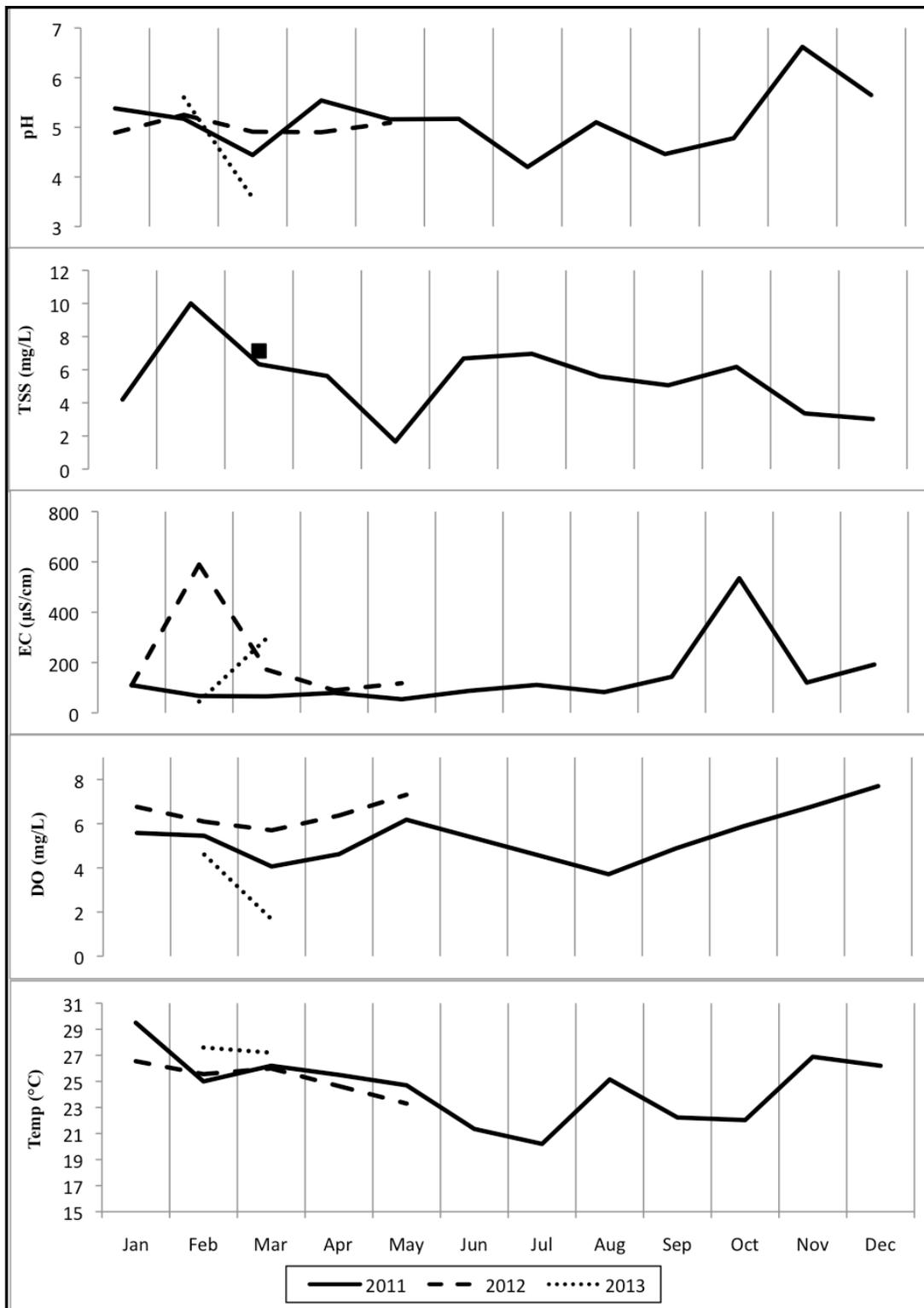
SCC2 Annual variations of water quality in the canal control point. Data combined for the previous canal control basin, SCC, and the current control basin, SCC2 for a more complete data set. Most complete data set relative to all other sampling sites.



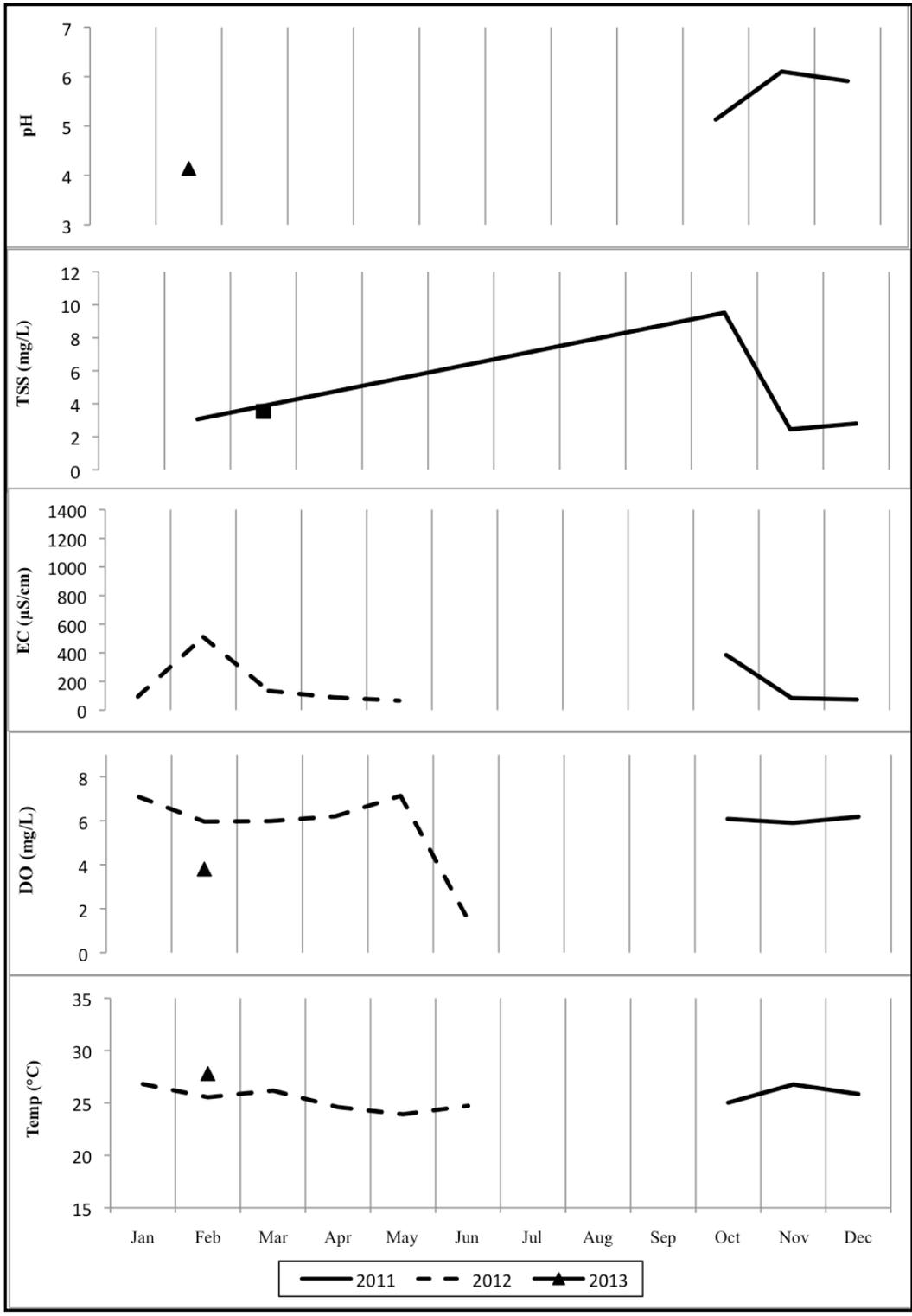
WMC 803 Annual variations of water quality at the new canal release points. WMC 803 was established as a second release point in October 2011.



WMC 703 Annual variations of water quality at the oldest running canal release point. WMC 703 was established as the first release point in February 2011.



S43 Annual variations of water quality at the discharge site for the tributary connecting WMC 703 to the Mandromondromotra River.



S44 Annual variations of water quality at the discharge site for the tributary connecting WMC 703 to the Mandromondromotra River.

APPENDIX B:*Raw data, averages, and standard deviation for water quality parameters***Table 1** Average values and standard deviation of hydrochemical compositions of all sites collected during April-May 2013. Values for S43 and S44 come from the QMM database for February 2013.

	Temperature (°C)	pH	Salinity (psu)	EC (µS/cm)	TSS (mg/L)	Turbidity (NTU)	DO (mg/L)	COD (mg/L)	SO ₄ ²⁻ (mg/L)	Ca ²⁺ (mg/L)	Al ³⁺ (mg/L)	Ni (mg/L)	Zn (mg/L)	NH ₄ ⁺ (mg/L)
WD90														
Average	25.630	6.300	0.080	174.300	4.020	3.180	2.420	64.500	2.729	0.841	0.066	0.008	0.002	0.010
SD	0.781	0.066	0.000	10.260	0.930	1.210	0.100	74.250	1.110	0.098	0.042	0.001	0.001	0.006
PADDOCK 3														
Average	26.260	3.670	0.400	819.000	6.600	8.620	2.430	9.500	276.880	49.720	8.365	0.146	0.095	0.010
SD	0.780	0.130	0.030	50.910	7.070	8.690	0.210	4.950	33.900	5.770	0.562	0.008	0.011	0.107
500M														
Average	25.440	3.710	0.390	808.330	57.100	63.620	2.700	70.500	267.760	49.264	9.649	0.131	0.110	0.010
SD	1.190	0.140	0.020	45.980	37.860	61.010	0.670	72.830	20.800	3.123	1.291	0.021	0.039	0.000
BASMIN														
Average	27.210	4.890	0.330	688.500	1373.200	1636.750	1.100	804.000	250.830	61.517	1.576	0.130	0.035	0.230
SD	0.370	0.950	0.010	23.330	1841.020	2161.270	0.370	1103.090	1.410	6.369	2.251	0.013	0.152	0.304
SCC2														
Average	27.320	4.160	0.350	720.000	4193.750	3299.250	1.440	115.000	268.670	60.663	5.707	0.154	0.096	0.150
SD	0.220	0.350	0.000	2.830	4240.170	3898.630	1.030	87.680	27.770	6.203	2.668	0.034	0.020	0.000
WMC 703														
Average	24.390	4.100	0.360	736.670	27.820	31.700	2.400	8.500	261.530	55.210	9.684	0.137	0.118	0.220
SD	1.240	0.140	0.000	11.590	31.990	20.840	0.200	6.360	43.250	6.443	1.476	0.036	0.004	0.358
WMC 803														
Average	26.290	3.700	0.210	446.670	28.770	37.050	2.400	19.500	116.380	13.846	6.114	0.042	0.051	0.140
SD	0.560	0.390	0.010	27.060	20.200	26.660	0.230	20.510	18.870	2.274	0.985	0.024	0.006	0.240
S43														
Feb-13	27.600	5.600	n.a.	45.000	7.130	4.050	4.600	6.000	4.840	1.190	0.090	0.007	0.002	0.100
S44														
Feb-13	27.800	4.140	n.a.	167.000	3.530	7.300	3.800	23.500	17.490	3.820	0.700	0.007	0.005	0.100

APPENDIX C:

Calculation of Pearson's Correlation Matrix (Gotway et al. 1994)

Pearson's r value, or the linear correlation coefficient, is the most commonly used correlation measure because it measures the linear association of two variables. Values range between -1 and 1. If two samples are completely, positively correlated (i.e. as one parameter increases in value, the other parameter increases in value) then the r value is 1. If the values are completely, negatively correlated (i.e. as one parameter increases in value, the other parameter decreases in value by the same magnitude) then the r value is -1. If there is no correlation, the r value equals zero.

Calculation of Pearson's r assumes the data follow a bivariate normal distribution; therefore, a case of increasing variance is not detected. The value is calculated using the following equation:

$$r = \frac{1}{n-1} \sum_{i=1}^n \left(\frac{x_i - \bar{x}}{s_x} \right) \left(\frac{y_i - \bar{y}}{s_y} \right)$$

where, the values are standardized by dividing the distance from the mean by the standard deviation of each variable x and y . The significance of r , using the test statistic t_r to determine its variance from zero, is then calculated using the following equation:

$$t_r = \frac{r\sqrt{n-2}}{\sqrt{1-r^2}}$$

Pearson's r is a dimensionless property, not affected by changes in scale or unit. The test statistic, however, is highly sensitive to outliers because it tests the linear relationship between two variables.

APPENDIX D:

Method for Agglomerative Hierarchical Clustering

Agglomerative hierarchical clustering (AHC) is a method of reducing data from many sites into smaller homogenous groups sharing similar water quality characteristics. AHC commonly uses a dissimilarity measure based on Euclidean distance and Ward's methods. The Ward's method clusters sampling sites by minimizing in-cluster variance through application of recursive algorithms to the initial squared Euclidean distance between individual sample sites (Ward 1963). The Euclidean distance at time t is calculated using the following equation:

$$dist_{ij}(t) = \left[\sum_{k \in P_t} (x_{ikt} - x_{jkt})^2 \right]^{1/2} \quad i, j = 1, 2, \dots, 19, 20$$

where, x_{ikt} is a value of the quality variable k measured at location i , P_t is the set of all water quality variables measured at both sites i and j .

Cluster analysis can be carried out using other normalizing methods, such as complete linkage (further neighbor) and average linkage (between and within groups); however, Ward's methods tend to result in a small spatial distorting effect, use more information on cluster contents, and yield the most meaningful clusters, relative to other clustering mechanisms (Willet 1987, Vega et al. 1998). The Ward's minimum variance method consists of the following calculation:

$$D_{ij} = \frac{\|\bar{x}_i - \bar{x}_j\|^2}{\frac{1}{N_i} - \frac{1}{N_j}}$$

where, D_{ij} is the dissimilarity measure between two clusters at site i and j , $\|x_i - x_j\|^2$ is the Euclidean distance (i.e. square root of the sum of the squares of the elements x at site i and j), and $N_{i,j}$ is the number of observations/samples at each site i and j (Ward 1963). In addition, AHC was adapted to account for missing salinity data for S43 and S44. The two missing points were replaced with the mean of salinity data from the other sites. There are many more explanations for AHC methods that go into further detail (Massart & Kaufman 1983; Gonçalves & Aplium 2011; Willet 1987).

APPENDIX E

Euclidean distance matrix (a) and cluster characteristics (b) for AHC

(a)

	1 (WD90)	2 (WMC703)	3 (SCC2)	4 (S43)
1 (WD90)	0	625.15	5365.87	142.00
2 (WMC703)	625.15	0	5295.62	740.62
3 (SCC2)	5365.87	5295.62	0	5378.37
4 (S43)	142.00	740.62	5378.37	0

(b)

Class	1	2	3	4
Objects	2	4	2	1
Sum of weights	2	4	2	1
Within-class variance	995.00	38473.31	5597729.27	0.00
Minimum distance to centroid	22.31	51.46	1672.98	0.00
Average distance to centroid	22.31	147.86	1672.98	0.00
Maximum distance to centroid	22.31	281.87	1672.98	0.00
	WD90 S44	Paddock 3 500M WMC703 WMC803	BASMIN SCC2	S43